COAL TAR COLOURS,

AND

RECENT IMPROVEMENTS

IN

DYEING AND CALICO PRINTING.

DR. F. CRACE CALVERT.

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LECTURES

ON

COAL TAR COLOURS,

AND ON

RECENT IMPROVEMENTS AND PROGRESS

IN

DYEING AND CALICO PRINTING,

EMBODYING COPIOUS NOTES TAKEN AT

The Last London International Exhibition,

AND

ILLUSTRATED WITH NUMEROUS PATTERNS OF FABRICS DYED WITH ANILINE AND OTHER COLOURS.

BY

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PHILADELPHIA:

HENRY CAREY BAIRD,

INDUSTRIAL PUBLISHER,

406 WALNUT STREET.

FIRST LECTURE.

I CANNOT presume to give, in a short course of lectures, a full account of all the improvements and inventions which must have occurred in such extensive trades as those of dyeing and calico printing, since the Exhibition of 1851, and especially during a period of extraordinary progress like that which has just passed. The utmost, therefore, that I can do is, to lay before you an outline of the principal discoveries which have come to *my knowledge* during the period under consideration.

I wish, however, to state that the processes of which I shall speak are those generally known to calico-printers and dyers; for it will be easily understood that many may use methods peculiarly their own, and that it would be a breach of confidence were I to publish any such processes that may have been communicated to me.

I shall divide the subject into two heads. First, treating of new dyeing materials obtained from well-known dyestuffs, and then of dyestuffs altogether new, together with their application to dyeing. Secondly, I shall consider the subject of calico printing.

Madder.—It is impossible within the limits of a Lecture to enter at any length into all the facts connected with this important dyestuff, the one, of all others, most extensively used in the arts of dyeing and calico printing, owing to the facility with which, by means of different mordants, a great variety of colours is obtainable, such colours being easily modified in tone, and resisting the action of light and most chemical agents. This valuable dyestuff, which is chiefly imported from France, Turkey, Italy, and Holland, is obtained from the *Rubia Tinctorum*. Our chemical knowledge of the composition of this root, was, up to 1851, in a most unsatisfactory state. Thus, whilst we find that MM. Decaisne, Jean Gerber, Edmund Dollfus, &c., asserted only one colouring principle, to which they gave the names of *alizarine*, *colorine*, or *azale*; others, such as MM. Persoz, Runge, &c., admitted two colouring principles, *alizarine* and *purpurine*, and Kuhlmann added to these two, a third, called *xanthine*. But Dr. Edward Schunck, F.R S., published, in 1851, his most valuable and extensive researches on the chemical composition of madder, which not only threw much light on the colour-giving principle of the rubia root, but also, as I will presently

show, led to valuable commercial applications. He adopted the view, that although the roots contained a certain quantity of colouring matter called alizarine, yet that the ultimate source of this only colour-giving principle was a substance to which he gave the name of *rubian*. He further found that one equivalent of this substance under the influence of a ferment called *erythrozym*, or of acids, or alkalies, would, by losing 14 equivalents of water, be converted into 4 equivalents of alizarine, as the following equation shows :—

$$\underset{\text{Rubian.}}{C_{56}\,H_{34}\,O_{30}} = 4\,\underset{\text{Alizarine.}}{(C_{14}\,H_5\,O_4)} + \underset{\text{Water.}}{{}_{14}HO}$$

This result satisfactorily explained the change of madder into garancine by the action of sulphuric acid on that root, from the fact that rubian was susceptible of conversion, under the same influences, not only into alizarine, but also into two valueless substances, called rubiretine and verantine. This led Mr. Simon Pincoffs, in conjunction with Dr. Schunck, in 1852, to the production of a most important dyeing material, called by them *commercial alizarine*. But to enable you to understand in what this product differs from garancine, and also its mode of preparation, it is necessary that I should state that the verantine and rubiretine are not colour-giving principles, and that they interfere with the beauty and brightness of the fine shades of purple given by alizarine, which, according to Dr. Schunck, is the only colour-giving principle contained in madder.*

Garancine, which, even before 1851, was extensively used for producing red, purple, and chocolate, upon calico, was obtained, as you are aware, either by mixing together at an ordinary temperature equal weights of madder and sulphuric acid, then adding water, when the garancine was produced, requiring only to be thoroughly washed so as to remove the acid;—or by mixing the roots with one-third their weight of sulphuric acid previously diluted with water, and carrying the whole to the boil for one or two hours, washing the residue repeatedly, and using, in the last operation, some alkaline carbonate.

Specimens of Garancine Styles.†

* Dr. Schunck also obtained as products of decomposition of rubian, rubianine and sugar. Those who are interested in these chemical researches will find them fully detailed in the Transactions of the Royal Society.

† We are indebted to Messrs. Wood and Wright for the above specimens.

Although garancine thus prepared gave colours similar to madder, yet they were wanting in solidity. This effect, especially as regards purples, was overcome by Messrs. Pincoffs and Schunck by taking principally garancine prepared as above, but thoroughly depriving it of acid, and submitting it to the action of high-pressure steam, when the substance called verantine is decomposed or modified so as to stain the whites less and not to interfere with the purple-dyeing power of alizarine. The advantages possessed by this product, which is now so extensively used in calico printing, that several millions of pieces have been dyed with it, are, as stated by Messrs. Pincoffs and Schunck, as follows :—It produces good lilacs economically and without soaping ; great promptitude and regularity in the production ; facility of producing combination of lilacs with catechu, lilac and chocolate, and lilac and orange, which results cannot be obtained so satisfactorily with madder or garancine ; production of lilac shades graduated *ad libitum* as to cost. Lastly, economy of mordaunts. I shall again refer to this in speaking of calico printing.

*Specimens of Alizarine Styles.**

Mr Higgins has lately devised a method of preparing commercial alizarine, which differs from that of Messrs. Pincoffs and Schunck, in that he boils garancine, carbonate of soda, or a little ammonia. The liquor, which is alkaline at starting, becomes acid after being boiled twenty-four hours, which converts the garancine into alizarine.

* Kindly supplied by Messrs. Pincoffs & Co.

Whilst on this class of madder products, I may refer to an improvement effected by Mr. John Lightfoot, in the manufacture of *garanceux* (discovered in 1843 by Mr. Schwartz), or spent adder, which has been treated with sulphuric acid, as above described, for the preparation of garancine. The method now generally followed is to collect the spent madder in bags as it runs from the dye-becks, and then throwing it on to a heap, to be ultimately converted into garanceux, by acting upon it as above described with sulphuric acid. Mr. Lightfoot, however, recommends large vats to be provided, allowing to run into them the hot spent madder liquors of the dye-becks, together with vitriol, leaving the whole to stand for 24 hours, running off the clear liquor and washing the solid garanceux thus produced until all impurities and acid are removed. The advantages claimed are, first, saving of fuel, by economising the heat of the waste liquors, and secondly, the production of one-fourth more colouring matter.

Having now laid before you an outline of the researches of Dr. Schunck, and briefly described the commercial product which resulted from them, as well as *garancine* and *garanceux*, also closely allied in their nature to *commercial alizarine*, I shall proceed to draw your attention to some scientific data, as well as practical results, both of which strongly tend to confirm the views of M.M. Persoz, Runge, &c., respecting the existence of two distinct colouring principles in madder, viz , *alizarine* and *purpurine*. According to these chemists, the following are the distinctive characteristics of these two colouring principles:—1. *Alizarine* gives with alkalies a beautiful violet solution, whilst *Purpurine* gives a bright red. 2. The alkaline solution of alizarine resists the action of the atmosphere, whilst that of purpurine does not. 3. Alizarine is nearly insoluble in a boiling solution of alum, whilst purpurine is freely soluble in that menstruum, yielding to it a fine pink colour. 4. The best process, however, to distinguish these two substances is that published in 1860, by Professor Stokes, of Cambridge, Secretary to the Royal Society, and which is so delicate that he states, in a letter to me, that he is able to detect the presence of purpurine in a solution of alum in which he had boiled one grain of dyed calico. Professor Stokes further states that in examining some specimens of cloth, one dyed with commercial alizarine and the other with garancine, he found the colouring matter of the first to be alizarine with a trifling quantity of purpurine, and of the second to be purpurine with a small quantity of alizarine ; so that according to this gentleman the garancine he examined might be called "commercial purpurine." He further states that he is quite satisfied that madder contains no other substance or mixture of substances possessing the optical properties which he observed as especially characterizing purpurine. I consider these original researches of Professor Stokes to be so new and important to the dyer and printer as to require the insertion here of an extract from a paper published by him in the *Memoirs of the Chemical Society*, vol 12.

"*Optical Characters of Purpurine and Alizarine.*—The optical characters of purpurine are distinctive in the very highest degree; those of alizarine are also very distinctive. The characters here referred to consist in the mode of absorption of light by certain solutions of the bodies, and occasionally in the powerful fluorescence of a solution. They are specially valuable because their observation is independent of more than a moderate degree of purity of the specimens, and requires no apparatus beyond a test-tube, a slit, and a small prism, a little instrument which ought to be in the hands of every chemist.

"*Alkaline solution of purpurine.*—If purpurine be dissolved in a solution of carbonate of potash or soda, (it is easily decomposed by caustic alkalies,) the solution obtained absorbs with greatest energy the green part of the spectrum. In this and similar cases it is necessary to take care either to use a sufficiently small quantity of the substance, or else to dilute sufficiently the solution, or view it through a sufficiently small thickness; otherwise a broad region of the spectrum is absorbed, and the peculiar characters of the substance depending on its mode of absorbing light are not perceived. If the solution be contained in a wedge-shaped vessel, the effect of different thicknesses is seen at a glance; but a test-tube will answer perfectly well if two or three different degrees of dilution be tried in succession. When the light transmitted through an alkaline solution of purpurine of suitable strength, after being limited by a slit, is viewed through a prism,

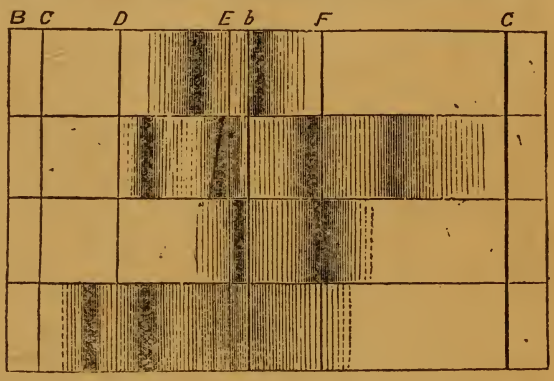


Fig. 1.—Solution of purpurine in carbonate of soda or potash, or in alum-liquor.

Fig. 2.—Solution of purpurine in bisulphide of carbon.

Fig. 3.—Solution of purpurine in ether.

Fig. 4.—Alkaline solution of alizarine.

two remarkable dark bands of absorption (Fig. 1) are seen about the green part of the spectrum, comprising between them a band of green light, which, though much weakened in comparison with the same part of the unabsorbed spectrum, is bright compared with the two dark bands, which latter in a sufficiently strong solution appear perfectly black. The places of the dark bands, estimated with reference to the principal fixed lines of the spectrum, are given in the figure.

"*Solution in a solution of alum.*—This solution has the same peculiar mode of absorption, and (Fig. 1) will serve equally well for it. But it has the further property of being eminently fluorescent, which the alkaline solution is not at all. The fluorescent light is yellow, but ordinarily appears orange from being seen through the fluid. The difference between the alkaline and alum-liquor solutions as to fluorescence does not depend on the acid reaction of the latter, but on the alumina. A solution exhibiting to perfection the peculiar properties of the alum-liquor solution may be obtained by adding to a solution of purpurine in carbonate of soda a solution of alum to which enough tartaric acid to prevent precipitation, and then carbonate of soda, has previously been added; and in this case the fluo-

rescent solution is obtained at once and in the cold. This forms a very striking reaction in a dark room, according to the method described in the *Philosophical Transactions for* 1853, p. 385, with the combination, solution of nitrate of copper and a red (Cu_2O) glass. Some other colourless oxides besides alumina develop in this manner fluorescence, though to a less degree."

Messrs. Schaaff and Lauth having exhibited in the French department of the late Exhibition some most beautiful commercial preparations obtained from madder, called by them Purpurine and Green Alizarine, I forwarded samples to Professor Stokes, who pronounced the alizarine to be composed almost entirely of that substance, with a dark green resin, which Emile Kopp considers to be produced by the decomposition of chlorogenine ; whilst the purpurine was declared by him to be that substance in a high degree of purity. As both these substances are now beginning to be extensively used by French printers, and to some extent by English houses, I cannot do better than give you an outline of Messrs. Schaaff & Lauth's process, as devised by the eminent chemist, Mr. Emile Kopp :—Six hundred pounds of ground madder are allowed to macerate for ten hours in a vat containing 800 to 1000 gallons of a solution of sulphurous acid, and after running off this liquor, the madder is again treated with 200 to 250 gallons of the same acid solution. These liquors are then mixed with three per cent of sulphuric acid, specific gravity 1 60, and the whole heated to about 100° by means of steam, when the purpurine separates itself under the form of large red flakes, which, in a few hours, settle at the bottom of the vat. The liquors are then run off, and carried to ebullition for three or four hours, when a new substance called green alizarine is liberated and precipitates. Both these products require only washing to be ready for the printer. The dyeing power of these new substances is remarkable, that of purpurine being equal to forty or fifty times the same quantity of madder, and the green alizarine to thirty-eight times that of madder. The 600lbs of madder yield about 4lbs. of purpurine and about 16lbs. of alizarine. The madder treated as above described, can be converted into garancine, the dyeing power of which is equal to half that of ordinary garancine. Green alizarine can be employed for the same purposes as commercial alizarine. Purpurine gives magnificent reds and pinks with alumina mordants, but no purple with iron mordants.

To Dye Wool or Silk with Purpurine.

The wool is mordanted in the ordinary manner as for garancine either with alum and cream of tartar, or with a solution of tin and tartar. The solution of tin which has hitherto given the best results is the following :—

300 parts	Nitric Acid	This mixture being placed in a cold water bath 50 parts of tin are added by degrees, until all is dissolved.
100 „	Water	
50 „	Sal-Ammoniac	

This solution is not ready for several days after filtration. To mordant wool it is dipped in a bath at about 80°, temperature, containing

a small quantity of the above solution, and the bath is raised during half an hour to about 186°. The wool is then removed and washed. It is then dyed wtth purpurine, in a bath containing the colouring matter, the temperature of the bath commenceing at 86° and rising to the boil in half an hour.

Or the following process may be substituted with advantage. Purpurine is neutralized with a small quantity of soda crystals, or carbonate of ammonia, by placing the purpurine in a vessel, and pouring boiling water upon it, to which the alkali is then added.

Wool mordanted with alum and cream of tartar gives a brilliant crimson red.

Wool mordanted with tartar and a solution of tin gives a scarlet almost as fine as that from cochineal.

From 30 to 50 grains suffice for a square yard of wool or merino.

To obtain a brilliant orange red, the wool is mordanted with tartar and tin solution to which has been added a little fustic or cuba wood. The whole is heated in a tinned boiler to 160°, and then washed. The wool is then dyed with purpurine as above directed. If the shade is not yellow enough, a little fustic may be added to the dye itself.

Although purpurine and alizarine differ considerably in some of their chemical reactions, as well as in the colours they yield with various mordants, still there is no doubt that they are closely allied to each other in their chemical composition, for Dr Schunck has proved that both these substances yield phthalic acid when decomposed by nitric acid; a property which belongs, as far as we know, to no other substance except napthaline, a white solid crystalline substance obtained from coal tar. Without entering into the observations made by Mr. Strecker on the relation subsisting between chloro-napthalic acid and alizarine, I cannot refrain from drawing your attention to a statement by Mr. Z. Roussin, who in 1861 startled the scientific world by declaring that he believed he had discovered the means of making from naphthaline the important colour-giving principle which I have already mentioned to you when speaking of madder, called alizarine, and what strengthened his belief was, that he thought he had succeeded in removing two equivalents of oxygen from binitronaphthaline, and transforming the nitrogen thereof into ammonia, leaving, as a residue, alizarine, as seen by his formula :—

Binitronaphthaline	$C_{12}\ H_6\ N_2\ O_8$
Minus oxygen	$-\ O_2$
Plus hydrogen	$+\ H^6\ H_2$
Equals	
Alizarine	$C_{12}\ H_6\ O_6$
Plus ammonia	$N_2\ H_6$
Plus water, ...	$2HO$

The simple process which he devised to obtain a crystalline substance which gave a red colour with an alumina mordant, consists in dissolving slowly binitronaphthaline in concentrated sulphuric acid, and raising

the temperature gradually to 392°, when he adds granulated zinc in successive small portions. After a short time sulphurous acid is given off, and the conversion of binitronaphthaline into a red colouring matter is effected. All that is now required is to dilute the liquor with eight or ten times its volume of water, and carrying it to the boil, filter, and allow the whole to cool, when M. Roussin's so-called alizarine deposits under the form of fine red or orange coloured crystals. Although this product possesses some properties similar to those of alizarine, it differs from it in many of its chemical reactions, and also because it does not furnish the purple and chocolate colours given by alizarine with iron, and iron and alumina mordaunts. Still these results, arrived at by M. Roussin, are so remarkable, that it is to be hoped that he will persevere in his endeavours to solve this interesting problem. Of late years the French calico printers have applied, for light styles of madder-pinks, extracts of madder, or garancine, which have generally been obtained by treating madders or garancines with alcohol or wood-spirit, and adding to them acetate of alumina and acetic acid; a similar process has recently been patented by Mr. F. A. Gutty. Another and most interesting process has recently been published by Mr. Emile Kopp, for the production of pure crystallized alizarine from garancine. It consists in submitting dry garancine in a double cylinder to the action of superheated and saturated steam, when the alizarine is carried off by the steam, and the whole condensed in a refrigerator.

Flower of Madder.—This product, which is now extensively used by continental printers, and which was introduced to the trade by MM. Julian and Roquer towards the beginning of 1852, is prepared by allowing madder to ferment, and then washing it thoroughly, which removes from it, not only all soluble matters such as sugar, mucilaginous substances, acids &c., which interfere with the fixation of the alizarine on the various mordants, but also (in accordance with Dr. Schunck's researches on the influence of the ferment erythrozym on rubian), increases the quantity of colour-giving principle or alizarine. It is found, by experience, that 100 parts of flower of madder are equal to about 200 parts of ordinary ground roots, and that the shades are finer, the pinks and reds also having greater solidity. Mr. E. Mucklow has recently patented a process similar to the above, which consists in alternately macerating and pressing madder roots so as to expel from them various materials which, as above stated, interfere with the dyeing of the fabrics.

Before leaving the subject of this valuable tinctorial substance, I think it advisable here to touch upon its most ancient, though frequently improved application, viz, that of *Turkey red dyeing*, so celebrated for the brilliancy and fastness of its colours, and any one who carefully examined the late Exhibition must have been struck with the great number of the specimens of this colour which appeared in almost every department, but especially in those of Prussia, Switzerland, and France.

Without entering into a full detail of the numerous and tedious manipulations undergone by the yarn in the course of its preparation for fixing the colouring principles of madder, it may be stated that the chief characteristic of Turkey-red dyeing, is the use of olive or Gallipoli oil as a fixing agent. The bleached yarn is first soaked in a peculiar quality of this oil—I say peculiar, because the oil used must, when mixed with a small quantity of an alkaline carbonate, form a white emulsion; this is due, as we now know from M. Pelouze's researches, to a ferment which the oil, as it is liberated from the berry, carries with it, and which resolves the oil into its component parts, viz., glycerine and fatty acids; and it is the oils so modified which are adapted for Turkey-red dyeing The yarns saturated with these acids are dipped into a solution of carbonate of soda, and then exposed to the action of the air, or air and steam in a warm room. After this treatment has been repeated a sufficient number of times, the yarns are passed through a solution of nut-galls, then into a solution of a salt of alumina, called red mordant, and the yarn so prepared is ready for dyeing, to effect which it is boiled for two or three hours in a bath to which madder-root has been added. Lastly, the brilliancy of the colour is completed by boiling the yarns in a strong solution of soap.

Indigo.—I have the pleasure again to draw your attention to a series of researches by Dr. Edward Schunck, and to enable you to appreciate the value of his discoveries in connection with this important dyestuff, it is necessary that I should first state that chemists held two different opinions as to the condition in which the colouring matter existed in the indigo plants. Thus, Chevreul, Girardin, &c., considered that the indigo contained in the plant was in the form of white, or de-oxygenated blue indigo; whilst Giobert and others believed that it did not pre-exist in the vegetable, but was formed during the process of fermentation, which is usually employed for the extraction of the colour from the *Isatis tinctoria* and *Indigofera anil.* Serious doubts having arisen in the mind of Dr. Schunck, whether either of these theories correctly explained the state in which indigo existed in the indigo plant, he undertook a long series of researches by which he was enabled to show, with a positive certainty, that the *Isatis tinctoria* contains a substance easily soluble in hot and cold water, alcohol, and ether, and which, by the action of strong mineral acid, yields indigo blue. Further, that the information of the colouring matter from it can be effected without the intervention of oxygen or of alkalies, and that the latter, indeed, if allowed to act upon it before the application of acid, entirely prevents the formation of the colouring matter; viz., indigo blue. To ascertain whether the substance which he calls *indican*, pre-existed in the plant, Dr. Schunck operated as follows:—He digested in ether some perfectly dry leaves of the *Isatis tinctoria,* removed the ethereal solution, and having exposed it to spontaneous evaporation, it left a green syrupy residue, from which water extracted *indiean,* for by the action of boiling sulphuric acid, it yielded an abundance of indigo blue. To obtain the

indican in a high state of purity, he found it necessary to treat the leaves with alcohol and ether, and to submit the extract to various chemical operations, to get rid of all impurities, so as to obtain indican as a yellow transparent glutinous substance, of a slightly bitter and nauseous taste. This substance presents the remarkable property (similar to that of rubian in madder) of being susceptible under the influence of a ferment in the plant, or of acids, of yielding indigo blue and sugar, as seen by the following chemical formula :—

$$\left.\begin{array}{l} \text{1 eq Indican } C_{52}\,H_{31}\,NO_{34} \\ \text{4 eqs Water } \quad H_4\,O_4 \end{array}\right\} = \left\{\begin{array}{l} C_{16}\,H_5\,NO_2 \text{ 1 eq Indigo blue.} \\ C_{36}\,H_{30}\,O_{36} \text{ 3 eqs Sugar.} \end{array}\right.$$

$$C_{52}\,H_{35}\,NO_{38} \qquad C_{52}\,H_{35}\,NO_{38}$$

To obtain this interesting decomposition with acids, it is simply necessary to heat the indican with strong sulphuric or hydrocloric acid, when the indigo blue precipitates while the sugar remains in solution. But indican is so liable to undergo modifications, that if the action of the acids be continued, besides the indigo blue an indigo purple is formed, called by Dr. Schunck *indirubine*. To fully appreciate the value of these researches it is necessary that I should lay before you an outline of the manufacture of indigo, as some of you may not be acquainted with it. Commercial indigo is obtained from plants belonging to the leguminous tribe, known under the general name of *indigofera*, which plants are mowed and placed in large vats with water, and allowed to ferment for 8 or 10 hours, when the supernatant liquor first becomes green and then blue. It is then run off into other vats and well agitated, so as to bring it thoroughly under the action of the atmospheric oxygen, when the white soluble indigo becomes thoroughly oxydised into blue insoluble indigo. A little lime water is now added and the whole left to settle, the deposit collected on a cloth, drained, pressed, divided into square lumps, and dried in the sun, when it constitutes commercial indigo. Dr. Schunck's researches show, as above stated, that under the influence of a ferment the *indican* is converted into sugar and white indigo; and they also explain that if the manufacturer is not extremely careful he may experience great loss in the amount of indigo obtained, for Dr. Schunck has observed that *indican*, when dissolved in water, is liable to undergo rapid modifications, and that instead of yielding by the acids indigo blue and *indirubine*, it gives *indiretine*, *indihumine*, &c. You will, doubtless, be struck with the great similarity which exists between the colour-giving principles of the madder and indigo plants, and with the light thrown upon this class of tinctorial matters by the laborious researches of Dr. Schunck.

To make indigo available for dyeing it is necessary to render it soluble, which is effected by the action of sulphuric acid on it. Two distinct preparations of indigo are found in commerce, viz.: the *acid sulphate of indigo*, and the neutral sulphate, *carmine of indigo*, or

sulpho-indigotate of soda, also called extract of indigo. To obtain the acid sulphate of indigo one part of finely pulverized indigo is gradually added to about eight parts of concentrated sulphuric acid, and care taken that the temperature does not rise beyond a maximum of 150° F. The whole is kept at that temperature for several hours, when it is mixed with a large quantity of water, to which has been added some chloride of sodium to render the sulphate of indigo insoluble. The whole is then thrown on filters, made of thick woollen blankets, which retains the sulphate whilst the impurities pass through. The washing of the pasty mass left on the flannel is continued until the washing liquor has lost all trace of the green colour which injures the beauty of the blue. To dye with the paste thus prepared, it is simply necessary to dissolve it in boiling water, and to dip wool in the solution, a beautiful blue shade being the result.

The carmine of indigo is prepared by neutralizing the excess of acid of the sulphate of indigo with carbonate of soda, when the sulpho-indigotate of soda thus formed becomes insoluble in the saline solution. The extract thus obtained is thrown on filters as above, and washed with a weak solution of chloride of soda until the impurities are removed. Superior qualities of these products have of late years been introduced into commerce by substituting for ordinary indigo, *refined indigo*, which has had a marked influence on the increased beauty and brilliancy of the shades of blue and green characterizing the dyed goods at the last Exhibition. To obtain this quality, two different processes may be followed. The first consists in treating finely pulverised ordinary indigo several times by strong muriatic acid, and applying a gentle heat so that the muriatic acid will not only dissolve the iron, lime, &c., which the indigo may contain, but also convert the amylaceous substance into dextrine or sugar, which is removed, together with the iron, lime, &c., by subsequent washing. The indigo is then further treated with a weak solution of caustic soda, which dissolves the chlorophyll and other organic impurities which pollute the indigotine. A still purer quality of indigotine may be obtained by adding to a large quantity of water, one part of finely pulverised indigo, two parts of sulphate of protoxide of iron (green copperas), and a quantity of caustic soda, slightly in excess of that necessary to neutralise the sulphuric acid of the copperas, carrying the whole to the boil and allowing it to settle, when the supernatant liquor is run off from the sediments and well agitated, in order to oxydise the white soluble indigo into the blue insoluble one, which is collected and dried. The insoluble sediment is treated several times with a weak solution of caustic alkali, in order to remove the whole of the indigotine which it may contain. Mr. Haeffly has drawn the attention of dyers to a beautiful preparation of sulphate of indigo which he calls sulpho-indigotic acid, and which he obtains by mixing one part of indigo with four parts of sulphuric acid, but instead of allowing these to remain for several hours together he throws them into a large quantity of water,

after they have been in contact only a short time, when the sulpho-indigotic acid falls as an insoluble depot, which is washed so as to remove the whole of the excess of acid. This product, mixed with a little hydrochloric acid and water yields to wool a most beautiful blue colour, which is transformed into a lavender or purple colour by passing the woollen fabric into a hot and weak solution of caustic alkali. To obtain the sulpho-purpurate of soda of Mr. Bolley, it is simply necessary to neutralise with carbonate of soda the sulpho-indigotic (or purpuric) acid of Haeffly. It is useless to take up your valuable time by describing the various well-known processes for dyeing wool, silk, &c., in indigo vats, although these processes have not lost their interest by age.

Orchil. It is hardly necessary for me to state that this dyestuff has been used for producing violets, mauves, reds, and other colours, for many years, and that the colouring matter was obtained by allowing lichens to remain in contact at natural temperature for several weeks with putrid urine and a little lime, and that of late years ammonia has been substituted for urine, with the addition of a little carbonate of soda, nitrate of soda, or alum. You are also doubtless aware that Robiquet was the first to obtain a colourless principle called *orcine*, and to show that under the influence of oxygen and ammonia it became transformed into water and a red colour called *orceine*, and that Dr. Schunck proved that a substance extracted by him under the name of *lecanoric acid*, from lichens, would, under the influence of heat and a solution of baryta, decompose itself into water, carbonic acid, and orcine. Without overlooking the interesting researches of Heeran and Sir Robert Kane on this subject, I must especially mention the labours and valuable researches of Dr. Stenhouse, which not only added greatly to our knowledge of the various chemical principles existing in lichens from which the orchil colouring matters are obtained, but also led him to discover a commercial method of extracting from the lichens the various organic substances capable of giving orchil colours when placed in favourable conditions. He also showed that the very small per-centage of colouring matters in proportion to the bulk of weed might be cheaply and commercially extracted in the locality where the lichens grow, thus saving the enormous expense of carrying a large bulk of useless matter from Africa and elsewhere to this country. If this valuable hint of Dr. Stenhouse's has not yet been acted upon as regards the saving of transport, his process for extracting the colour-giving principle has of late years been extensively adopted by manufacturers of orchil, enabling them to obtain cheaper and better colours from lichens. But still none of these advantages led manufacturers to the great desideratum of giving fastness to the beautiful purple shades obtained from orchils, until 1856, when Mr. Marnas, of the firm of Guinon, Marnas, and Bonnet, of Lyons, found that by treating lichens, as suggested by Dr. Stenhouse, with milk of lime, filtering

the lime liquor off and precipitating the colour-giving principle from it with hydrochloric acid, gathering these on a filter, and after having properly washed them, dissolving them in caustic ammonia, and keeping this ammoniacal liquor at a temperature of 153° to 160° for 20 to 25 days, when under the influence of that temperature, the colour-giving principles of the lichens fix ammonia and oxygen and are transformed into a new series of products; these Mr. Marnas separates from the coloured liquid by adding chloride of calcium, which causes a fine purple lake to be deposited, which, after being well washed and dried, is sold under the name of *French purple.* It is easy to understand that the chloride of calcium can be replaced by salts of alumina, tin, &c. What characterises this orchil colour from those previously known is, that it dyes animal fibres with greater facility than the common orchil, that it gives directly mauve colours, which can be modified by adding to them a little carmine of indigo, roseine, &c.; but the essential difference of these purples and mauves from ordinary orchil colours is—that while the latter are destroyed by acids and light, those of Mr. Marnas, on the contrary, withstand their action.

To dye silk or wool with French purple it is simply necessary to mix the lake with its weight of oxalic acid, boil with water and then filter, the oxalate of lime remaining on the filter while the colour passes in the filtrate. This liquor is then added to a slightly ammoniacal liquid contained in the dye-beck; all that is now necessary is to dip in the beck, silk, wool, cotton, mordaunted with albumen, or cotton prepared for Turkey red, when any of these materials will become dyed with magnificent fast shades of purple or mauve.

Silk dyed with French Purple.

It is a curious coincidence that after many years of anxious search, two purples from widely different sources should have been first discovered in the same year (1856) in different countries. I allude to Mr. Perkin's purple from coal tar, to which I shall refer further on.

Catechu, or *Terra Japonica*, which is extracted from the wood of the acacia catechu, and which we import in large quantities from the East Indies, is daily becoming of increased importance, owing to the great variety of colours that can be obtained with it. It contains two very distinct substances, a tannin (studied by Mr. Stenhouse) which gives a green precipitate with salts of per-oxide of iron, and also a substance called *catechine*, which under the influence of alkalies and oxygen is rapidly transformed into two acids called japonic and rubinic acid. As in catechu, the tannin gives various shades of drab, the catechine giving, with proper metallic salts, salmon, red, and wood colours. Some calico printers have of late, under my advice, washed with cold water pulverised catechu, which dissolves freely the tannin, leaving the catechine insoluble in cold water, this, however, being soluble in hot water, becomes

susceptible of application. Mr. Saac has recently published an interesting observation on the action of sulphuric acid upon catechu, shewing that it is decomposed principally into glucose and a brown resin, which brown resin when dissolved in moderately strong sulphuric acid or a solution of an alkali, assumes a beautiful purple colour, remarkable for its stability, and which will doubtless be employed with advantage as a substitute for catechu in the various applications of that substance in dyeing and printing.

Aloes.—Owing to the interesting researches of Drs. Schunck and Stenhouse upon the resin obtained from the *aloe socotorina*, and imported from the East and West Indies as well as Africa, the various colouring matters obtained by them have, of late, been employed by the French dyers for producing pinks, violets, maroons, and other shades.

Lac Dye.—Messrs. E. Brooke and Co., of Manchester, have introduced into commerce a lac dye superior to that imported from India, which, as you are aware, is prepared from stick lac. Their improvement consists in treating stick lac with weak ammonia, and adding to this solution chloride of tin, when a fine red insoluble matter is formed which precipitates. This is collected, and is ready for use.

Chlorophyll.—For many years attempts were made to fix upon fabrics the green coouring matter of leaves, but unsuccessfully, until, in 1854, MM. Hartmann and Cordillott, of Mulhouse, succeeded by the following simple process in obtaining on silk, wool, and cotton, fine green brilliant and solid colours. After having boiled a quantity of grass, so as to remove everything soluble in boiling water, it was heated with a hot caustic lye of specific gravity 1·03, this alkaline solution being then neutralized with hydrochloric acid, a fine green precipitate was thrown down. This precipitate was then dissolved in a solution of caustic lye, to which had been previously added some phosphate of soda and oxide of tin.* This mixture, properly thickened with gum, was printed and fixed by steaming. No doubt, by a slight modification in the *modus operandi*, this colour might be applied to dyeing.

Chinese Green, called *Lo-kao.*—In 1851 and 1852, public attention was drawn, by several English gentlemen, to samples of a green colouring matter, imported from China; and in 1853, Messrs. Guinon, of Lyons imported such quantities of the material as to enable them

* Any one who wishes for further information on the green colouring matter from plants, will find a most interesting paper by M. Fremy, published in the *Comptes Rendus* of the French Academy, for 1860, volume 50, in which that chemist shows that chlorophyll is composed of two colouring matters called phylloxanthine and phylloxcyanine.

to dye silks for the requirements of the trade. The silks so dyed by them, under the names of *Vert-Venus*, *Vert-Azof*, and *Vert Lumière*, were especially admired, from the beautiful green shades they assumed in artificial light; and although the price of the dye fell from £21 per pound in 1853, to £4 in 1860, these beautiful shades of green (especially in artificial light) have almost disappeared from the market, owing to the two following reasons:—first, their want of stability; and, secondly, because Messrs. Guinon, Marnas, and Bonnet, have found the following means of producing, at less cost, shades of green which also maintain this character under the influence of artificial light, *i.e.* by first dyeing their silks in Prussian-blue, and then dyeing them in an acidulated bath of carboazotic, or picric acid.

Vert Lumière.

It is an interesting fact to observe that, while the greens produced by indigo and picric acid appear blue in artificial light, those produced as above, with prussian-blue and picric acid, appear green under the same conditions. I cannot leave this interesting subject without making two further remarks:—first, Lo-kao is the only substance with which I am acquainted capable, with proper reagents, of producing the seven colours of the spectrum; secondly, that thanks to the advanced state of chemical and botanical science, we have succeeded in producing, in Europe, the identical substance imported only a few years ago, as a great novelty, from China—and for which, but for those sciences, we should still probably have remained tributary to that empire. Thus Mr. Charvin, of Lyons, has been able to obtain Lo-kao from a weed indigenous to Europe, viz., *Rhamnus catharticus*, for which he has received, from the Chamber of Commerce of Lyons, a gold medal worth 6,000 francs.* Samples of this were to be seen at the late Exhibition.

Murexide, or *Roman Purple*.—The colour to which I am now about to draw your attention furnishes another example of the assistance which the progress of chemical science has rendered to the art of calico printing. In 1776, the illustrious Swedish chemist, Scheele, discovered, in human urine, uric acid. In 1817, Brugnatelli found that nitric acid transformed uric acid into a substance, which he called *erythric acid*, but which was subsequently called, by Wöhler and Liebig, *alloxan*. In 1818, Dr. Prout found that the latter substance gave, when in contact with ammonia, a beautiful purple red colour, which he called purpurate of ammonia—the product known by the name of *murexide* since the researches of Liebig and Wöhler, published about 1837. These discoveries remained dormant in the field of pure science until the year 1851, when Dr. Saac observed that when alloxan came in contact with the hand it tinged it red. This led

* For full details on this subject, see Report presented to the Chamber of Commerce, at Lyons, by the Rev. Hélot, M. Persoz, &c.

him to infer that alloxan might be employed to dye woollens red, and further experiments convinced him that if woollen cloth were prepared with a salt of tin, passed through a solution of alloxan, and then submitted to a gentle heat, a most beautiful and delicate pink colour resulted. In 1856, MM. Depouilly, Lauth, Meister, Petersen, and Albert Schlumberger, applied it as a dyeing material to silk and wool, and succeeded in obtaining red and purple colours, by mixing the murexide with corrosive sublimate, acetate of soda, and acetic acid. For printing, a mixture of murexide with nitrate of lead or acetate of zinc, properly thickened, is applied on cotton fabrics, which are then allowed to dry for a day or two, when the colour is fixed by passing them through a mixture of corrosive sublimate, acetate of soda, and acetic acid. The Roman purple style of printing has been carried out extensively by Messrs. Edmund Potter and Co.; Boyd, Sons, and Hamel; James Black and Co.; and Littlewood and Wilson.

No doubt you will wonder whence such quantities of uric acid, or murexide, could be drawn to supply a demand like that which has arisen. This result has been achieved by the following process of extracting uric acid from Peruvian guano. Guano is treated repeatedly with hydrochloric acid, until all soluble matters are removed by heat and washing. The insoluble mass, which consists chiefly of sand and uric acid, is carefully treated with nitric acid of specific gravity of 1·40. When the action of the acid is completed, the mass is treated with warm water, and thrown on a filter. The filtrate, which has a yellowish colour, and contains alloxan, &c., is evaporated carefully to such a degree, that when left to cool it becomes a brownish red or violet solid, called by the inventor, *carmin de pourpre*, which is the substance chiefly used for printing, as above described. It is to the enterprising commercial spirit of Mr. Robert Rumney, chemical manufacturer, of Manchester, that is due the extensive production and application of murexide in this country.

Doubtless you are aware that alum, and cream of tartar, are used largely as mordaunts in the dyeing of silk, wool, and cotton, and that the latter substance has much risen in price, owing to the failure of the wine crops of late years; therefore, any process for economising the use of cream of tartar is a matter of importance. I am happy to state that Mr. Kuhlmann has, within the last few weeks, published in the Memoirs of the French Academy, a paper in which he furnishes a means of attaining that end. Having first confirmed a most important observation of Mr. Chevreul's, viz, that when cream of tartar is used as a mordaunt it is decomposed into tartaric acid, which adheres to the fibre, and into a neutral tartrate which remains in solution and is lost, and that if, on the contrary, instead of using the cream of tartar as a mordaunt, it is first decomposed into tartrate of baryta, and that this salt be used as a mordaunt, in connexion with a little hydrochloric acid, the two equivalents of the tartaric acid of the cream of tartar become available,

and consequently a saving of one-half the quantity of cream of tartar formerly used is effected.

In the hope that it may prove interesting to the members of this Society, I will now give some details respecting a few new processes for dyeing silk, before proceeding to treat of coal tar colours.

Catechu Black.—The silks are first passed into a solution of salts of peroxide of iron, then into a hot soap solution containing an excess of soap, from whence they are passed into a slightly acid bath of prussiate of potash. The silks which have thus been dyed Prussian blue, are dipped in a solution of persalt of iron, having a specific gravity of 1·15, the object of which is to give an iron mordaunt to the silk. They are then thoroughly washed and passed into a bath of catechu for organzine at 203°, and for tram at 172°, the silks being worked in this bath until it is cold, so as to saturate thoroughly the iron mordaunt with the colouring principle of catechu, and thus produce a black. They are then wrung on the peg and exposed to the atmosphere for 24 hours, after which they are passed into a soap solution at 150°, washed thoroughly, and the organzine is then dipped in a bath of weak acetic acid, and the tram in one of weak hydrochloric acid; finally, the silks are passed through an emulsion of oil, well worked on the peg and allowed to dry. These last operations are intended to remove, by means of the fatty matters, the harshness which the silk would otherwise possess. Whilst speaking of black silks, I may mention that public notice was drawn at the Exhibition to some samples shown by M. Gilet, of Lyons, which were dyed with a substance from Algiers, called *le Hennée des Arabes,* with which substance a superior weighted black silk is obtained.

The following is a process for preparing dyed silks, so that when woven into fabrics these will be fit for taking the moire antique:—Two parts of pure olive oil are mixed with one of concentrated sulphuric acid, and agitated until sulphurous acid begins to be liberated. It is then well mixed with 15 parts of lukewarm water, and the whole further diluted with boiling water. The silks are then passed into this bath and then into a second similar bath, to which has been added a little free vitriol. After this, they are successively dipped in a hot bath containing a little citric acid, then in the previous No. 2, to which is added a little sulphate of alumina and a little black dye to restore to the silk any colour it may have lost during the former operations. The silks, after having been dried in the air, are ready for weaving. The object of these processes is to introduce into the silk fatty acids, the property of which is to communicate to the silk a great degree of softness, and adapt it to receive, by intense pressure, the intended moire.

I will now describe a process for dyeing silks white. The silks, after having been boiled, are first passed into a slightly ammoniacal bath, and from thence into another of water, in which has been dis-

solved a little French purple, and lastly into another bath containing lukewarm water, to which is added, in successive portions, some carmine of indigo, and the silks are then dried. Many of you will doubtless remember that in my papers read here in 1851, I explained that, when the three primitive colours of the spectrum are mixed in due proportions, they produce white if reflected, and black if absorbed. The French purple gives the red; the carmine of indigo blue; and the silk itself the required yellow.

Several improvements have also taken place in the production of maroons, greens, and Prussian blues, but time will not allow of my laying the details before you.

SECOND LECTURE.

COLOURS DERIVED FROM COAL TAR.

THESE colours possess great interest, not only for their beauty and brilliancy but also on account of the source from whence they are derived, and present a remarkable instance of the services which abstract science frequently renders to the material interests of society. The discovery and application of these brilliant and enduring colours to dyeing and calico printing, may be said to constitute the chief distinction in this department of the arts, between the Exhibition of 1862 and that of 1851, and it will be highly interesting to trace the various scientific steps which have culminated in such remarkable results, that a substance which was originally, and so recently as 1826, a purely scientific product, has become, by a series of discoveries, the source of some of the most valuable dyeing materials. Thus, in 1825 Faraday obtained, for the first time, benzine from coal gas. In 1826 Unverdorben discovered a substance which was ultimately named aniline by Fritsche, and subsequently found by Dr. A. W. Hofmann as a product of coal-tar; and finally, by the researches of eminent chemists, the *benzine* of Faraday has become the *aniline* of Hofmann.

There can be no doubt that it is to the interesting and learned researches of Dr. Hofmann on aniline, that we owe the possession of these splendid colours, and further, it was one of his pupils, Mr. W. A. Perkin, who produced for the first time, on a commercial scale, aniline. and then the splendid purple colour which it is susceptible of yielding. Before describing to you the process patented by Mr. Perkin in 1856, to produce his purple, allow me to lay before you an outline of the present plan followed for obtaining aniline. The carburetted hydrogen, called "Benzine" (C_{12} H_6), and obtained by the careful distillation of purified coal naphtha at a temperature of about 186°, is treated with strong nitric acid, when a violent action ensues, which gives rise to nitrobenzine or C_{12} H_5 NO^4. To convert this compound into aniline, the following simple and practical process, devised by M. Beschamps, is adopted:—one hundred parts of nitrobenzine are mixed with an equal quantity of acetic acid, and 200 parts of iron filings, heat is produced, and the following chemical action ensues:

$$\underset{\text{nitrobenzine.}}{C_{12}\,H_5\,NO_4} + 2\,H\,O + 4\,Fe = 2\,(Fe_2\,O_3) + \underset{\text{aniline.}}{C_{12}\,H_7\,N}$$
water. iron. oxide of iron.

The mass when cool is introduced into a retort, and the raw product which passes from it is mixed with a little alkali or lime, and again

distilled, when aniline is obtained. This important substance is a colourless fluid, which boils at 359°, has a decided alkaline reaction, and sp gr. of 1 028.

Purple from Aniline.

As a purple was the first colour commercially produced from aniline, and applied for dyeing purposes, and as the process then patented by Mr Perkin still remains one of the best for producing that colour, I cannot do better than quote Mr. Perkin's own description of the process, as well as of the properties of his purple, as given by him in a paper read at the Chemical Society, in 1861:

"The method adopted for the preparation of aniline purple is as follows:—Solutions of equivalent proportions of sulphate of aniline and bichromate of potassium are mixed and allowed to stand till thrown on a filter and washed with water, until free from sulphate of potassium. It is then dried. This dried product is afterwards digested several times with coal-tar naphtha until all resinous matter is separated, and the naphtha is no longer coloured brown. After this it is repeatedly boiled with alcohol to extract the colouring matter. This alcoholic solution when distilled leaves the colouring matter at the bottom of the retort, as a beautiful bronze-coloured substance."

"The aniline purple prepared according to the process just described, although suitable for practical purposes, is not chemically pure. If required pure, it is best to boil it in a large quantity of water, then filter the resulting coloured solution, and precipitate the colouring matter from it by means of an alkali. The precipitate thus obtained should be collected upon a filter, washed with water until free from alkali, and dried. When dry it is to be dissolved in absolute alcohol, the resulting solution filtered, and then evaporated to dryness over the water bath.

Thus obtained, aniline purple appears as a brittle substance having a beautiful bronze-coloured surface; but if some of its alcoholic solution be evaporated on a glass plate, and viewed by transmitted light, it appears of a beautiful bluish violet colour. If considerable quantities of an alcoholic solution of the colouring matter containing a little water be evaporated to dryness, the surface of the colouring matter next to the evaporating dish, often exhibits a golden green appearance when detached.

Aniline purple is with difficulty soluble in cold water, although it imparts a deep purple colour to that liquid: it is more soluble in hot water; but its hot aqueous solution, when left to cool, assumes the form of a purple jelly. It is very soluble in alcohols, though nearly insoluble in ether and hydrocarbons. Aniline dissolves it readily. In properties it seems to be slightly basic, as it is more soluble in acidulated than in pure water. Alkalies and saline substances precipitate it from its aqueous solutions as a dark purplish black powder. Bichloride of mercury precipitates it in a very finely divided state. A little of this precipitate (which appears to be a double compound of chloride of mercury and colouring matter) when suspended in water, and viewed by transmitted light, appears of a blue or violet colour.

A small quantity of hydrate of potassium or sodium added to an alcoholic solution of the colouring matter causes it to assume a violet tint, but without effecting any change in the colouring matter itself. Ebullition with alcoholic potash does not decompose it."

Perkin's Purple.

Aniline purple dissolves in concentrated sulphuric acid, forming a dirty green solution which, when slightly diluted, assumes a beautiful blue colour; excess of water restores it to its original purple colour. It may even be heated for an hour to 100°C. with Nordhausen sulphuric acid without suffering decomposition, being restored to its original colour by means of water, and possessing precisely the same properties it had before being subjected to this powerful agent. Hydrochloric acid acts upon it in the same manner as sulphuric acid. It is decomposed by chlorine, and also by fuming nitric acid. Bichloride of tin is without action upon it.

Powerful reducing agents have a peculiar action upon this colouring matter, somewhat analogous to the action of reducing agents on indigo. An alcoholic solution of sulphide of ammonium mixed with an alcoholic solution of aniline purple, causes it to assume a pale, brownish tint. This solution, when brought in contact with the atmosphere, instantly recovers its original beauty and intensity of colour. An alcoholic solution of the colouring matter mixed with a little protoxide of iron, changes to a pale brown colour. This solution also becomes purple when exposed to the action of the atmosphere; sulphurous acid does not affect the colour of this substance.

Aniline purple forms a remarkable compound with tannin. When an aqueous solution of it is mixed with a solution of tannin, precipitation takes place. The precipitate thus formed after having been well washed, no longer possesses the properties of the pure colouring matter. It is insoluble in water. Like the pure aniline purple, it dissolves in concentrated sulphuric acid, forming a dirty green liquid; but on adding an excess of water to this solution, the new compound is precipitated unchanged; this compound is rather duller in colour than the pure colouring matter itself."

Without wishing to detract in the least from Mr. Perkin's merit in discovering and perfecting this important invention, it is due to two gentlemen, who laboured for some time with me, with a view of producing colours from the aniline, obtained directly from coal tar by Dr. Hofmann's process, to state that as early as the commencement of 1857, Mr. Clift, Mr. Lowe, and myself succeeded in producing purple and red colours by oxydising aniline by means of peroxide of manganese, bichromate of potash, or nitric acid, and during our researches on the methods of purifying these colours we found that tannin would precipitate them; and with these tannates dissolved in acetic acid we dyed specimens of silk, wool and cotton, which were exhibited at my lecture before the Society of Arts, early in 1858.

The application, however, of Mr. Perkin's purple remained extremely limited until the spring of 1859, at which time the extensive employment on the continent, of Messrs. Guinon, Marnas, and Bonnet's French purple (described in my former lecture), brought into fashion the mauve colour, and led to an enormous demand in this country for the aniline purple. The result was, that several parties commenced to seek for new methods of manufacturing the dye, and amongst these I may notice the following:—

Messrs. Depouilly and Lauth's method* (patented in June, 1860), consisted in adding to a salt of aniline a solution of chloride of lime, which yielded a purple insoluble precipitate which was repeatedly washed in slightly acidulated water, dissolved in concentrated sulphuric acid, and reprecipitated by the addition of a large quantity of water to the solution; it was then simply necessary to thoroughly wash the precipitate to render it fit for use when dissolved in alcohol or methylated spirit. Messrs. Beale and Kirkham also patented this process in 1859. Mr. Kay, in January, 1860, took out a patent for producing purple aniline, called *harmaline*, by adding to sulphate of aniline some peroxide of manganese, and heating the whole to 212°, when the harmaline so produced remained in solution, and was separated from an insoluble depot. The dissolved colour was precipitated by adding to the solution ammonia, sufficient to neutralize the acid, after which the insoluble colour was washed, dried and dissolved in methylated alcohol.

In January, 1860, Mr. Greville Williams patented the right of using permanganate of potash as a means of oxydising aniline, and producing purples and other colours. At about the same period Mr. D. Price took out a patent for acting on sulphate of aniline by means of the peroxide of lead.

On the 12th January, 1861, another interesting process to obtain aniline purple was patented by Mr. Adam Girard. Pure red aniline (known in this country as magenta), is mixed with an equal weight of aniline, and the mixture heated for several hours to 329°, when the mass is changed to a fine purple colour, requiring only to be mixed with water, and hydrochloric acid, to remove any aniline or red dye in excess, leaving the purple insoluble, but on being well washed with water, this becomes soluble in alcohol, acetic acid, wood naptha, and boiling water slightly acidulated with acetic acid. The above process has, I believe, been successfully worked by Messrs. Renard Frères, of Lyons, who call the product *Violet Imperial.*

Dale & Caro's Purple. Messrs. Dale and Caro patented, in 1860, the following interesting process for preparing purple aniline. One equivalent of a neutral salt of aniline is mixed with six equivalents of perchloride of copper and chloride of sodium, dissolved in as much water as is equal to 30 times the weight of the aniline used. A dark precipitate is formed during the ebullition of this fluid, which is thrown on a filter and washed with a weak solution of an alkali or alkaline carbonate, the colour being extracted by means of boiling water; it is then reprecipitated by a small amount of alkali and dissolved in methylated spirit †

In 1862, Mr. G. C. Nicholson secured a patent for producing a very

*These gentlemen have availed themselves of a reaction first noticed by Mr. Runge several years previously.

† The black matter left on the filter is now sold by Messrs. Roberts, Dale, & Co. to Printers, to be used as a pigment.

beautiful purple, called *Regina purple*, and as this dye has been largely used of late by dyers and printers, I think it desirable to give you a full description of his patent.

"I take red dye, such as is made from aniline or its homologues, and without the admixture of either aniline or its homologue I heat it carefully in a suitable apparatus to a temperature by preference between 390° and 420° Fahrenheit, the substance quickly assumes the appearance of a dark semi-solid mass, the red dye being transformed into a dark substance with evolution of ammonia, the mass I prefer afterwards to extract with acetic acid, using a quantity of acid about equal in weight to the amount of red dye treated, and this acid I dilute with enough alcohol to make a dye of convenient commercial strength. The solution obtained is of a deep violet or purple colour, and may be used directly for dyeing purposes.

*Regina Purple.**

What I claim is the producing a violet or purple colour from red dye, such as is made from aniline or its homologues by carefully treating it as described without admixture either of aniline or its homologue."

I cannot terminate this outline of the history of aniline purples without mentioning that Mr. J. Stark has lately patented a method of producing this colour by boiling for two or three hours a mixture of a salt of aniline with red prussiate of potash, leaving the whole to cool, when a grayish blue precipitate settles at the bottom. It is, however, not advisable to occupy your time with further details of this process, because I am not aware whether the colour obtained by it can compete with those already used, and also because the use of red prussiate of potash for producing aniline purple was mentioned by Mr. Emile Kopp previously to the date of this patent.

Rosaniline, or red colour from aniline.

The production of this brilliant colour, popularly known as magenta, was first observed by Mr. Natanson, in 1856, but more especially by Dr. Hofmann, when preparing carbo-triphenyl-triamine by the action of tetra-chloride of carbon on aniline, and although this eminent chemist did not further investigate its production, there can be no doubt that it is to his researches that the introduction of magenta into commerce is chiefly due; for it is easy to show that Mr. Verguin's substitution of anhydrous bichloride of tin for the chloride of carbon, was an obvious inference from Dr. Hofmann's observations. The best proof of the correctness of this view is that Dr. Hofmann's process has been further developed by M. Gerber-Keller, and is now in practical opera-

* Kindly supplied by Messrs. E. Brooke & Co.

*Dr. Hofmann's Magenta.**

tion at Mulhouse. The process consists in heating together under pressure at a temperature of about 347° three parts of aniline with one of bichloride of carbon; after several hours a brown red mass is formed, which is then treated with water evaporated to dryness, and the resulting colour dissolved in alcohol. It is by this method that the beautiful colour of the annexed specimen was obtained.

I have been informed that Messrs. Monnet and Dury, of Lyons, manufacture rosaniline by the above process, and purify the residue from the water solution before dissolving it in alcohol, by washing it with a little benzine. Before, however, giving you an outline of the processes which have been and are followed to obtain this colour commercially, I will bring under your notice Dr. Hofmann's complete and exhaustive researches on the composition of rosaniline, which are so remarkable not only for the light thrown on the general composition of the aniline colours, but also because several of the most eminent chemists of Europe had vainly endeavoured to unravel the composition of magenta. Omitting the chemical details contained in Dr. Hofmann's paper (which may be found in the Chemical News, vol. 5, 1862), I may state that the substance which gives the magenta colour is itself perfectly colourless, until it is combined with an acid such as hydrochloric, nitric, acetic, &c., when it becomes red; thus *roseine* is the acetate, *azalèine* the nitrate, and *fuchsine* the hydrochlorate, of rosaniline.

It is easy to prove that these coloured salts of rosaniline contain the colourless alkaloid, rosaniline, by adopting Dr. Hofmann's process, viz.:—By boiling, for instance, roseine with a large excess of ammonia, when the greater part of the base is precipitated in the form of reddish crystals In removing the ammoniacal liquor from this precipitate and allowing it to cool, the remainder of the rosaniline deposits in perfectly colourless crystals. Rosaniline, composed as follows:—

$$C_{20}\ H_{10}\ N_3\ H_2\ O$$

is a powerful and well defined base, susceptible of combination with one, two, or three equivalents of acid, but the salts with one equivalent of acid are those most readily formed, and which crystallize with the greatest facility. Most persons must have admired, in the recent exhibition, the beautiful crowns of acetate of rosaniline exhibited by Messrs. Simpson, Maule, and Nicholson, which presented in reflected light the green metallic lustre of cantharides' wings. This acetate of rosaniline, or roseine, appears to be the salt of this base which is generally preferred by dyers and calico printers, at least in this country. During the researches of Dr. Hofmann on roseine, he made the curious observation that if rosaniline was submitted to the action of reducing agents, such as hydrogen in a nascent state, two equivalents of

* Supplied by M. Gerber-Keller.

hydrogen were added to it, and a new substance called *Leucaniline* (C^{20} H^{21} N^3) was formed, the composition of which bears the same relation to that of rosaniline, as the composition of white indigo bears to that of blue. Dr. Hofmann has published several highly interesting papers upon the coal-tar colours, to each of which I shall draw your attention as we proceed, and in the meantime I will lay before you the principal processes which have been devised and carried out for producing magenta commercially.

The first commercial production of this colour was made by Mr. Verguin, of Lyons, who employed, as stated above, anhydrous bichloride of tin, and whose mode of preparation was patented in April, 1859, by Messrs. Renard Frères, of Lyons, who gave the name of *Fuchsine* to the product. Into a glazed iron pan are introduced 100 parts of aniline and 60 parts of anhydrous bichloride of tin, and the whole is heated for 15 or 20 minutes, at a temperature of about 392°. The dark red liquor thus produced is left to cool, when it becomes thick and glutinous; it is then mixed with boiling water and the solution filtered; to the filtrate is added chloride of sodium, which determines the precipitation of fuchsine, which, when dissolved in methylated alcohol, is ready for use.

Roseine was first introduced into the trade early in 1860, by Messrs. Simpson, Maule and Nicholson, and manufactured by them according to the following process, patented by Mr. D. Price, in 1859. The process consisted in boiling a solution of one equivalent of sulphate of aniline with two equivalents of binoxide of lead; the red coloured solution thus obtained was filtered, and the filtrate evaporated to a small bulk, when a resinous matter separated. To the solution was then added an alkali, which threw down the colouring matter which was washed and dried. It was then simply necessary to dissolve it in methylated alcohol to render it fit for use. These manufacturers, however, shortly afterwards became possessors of Dr. Medlock's patent for the production of magenta, by means of arsenic acid, and as this substance appears to be the best adapted for the manufacture of roseine, I think it advisable to give a detailed account of the process.

Although the use of arsenic acid was mentioned in a patent taken out by Mr. Gerber-Keller on the 10th December, 1859, still the first patent containing a description of the mode of employing that substance was that of Dr. Medlock, dated 18th January, 1860, in which he states,—"I mix aniline with dry arsenic acid, and allow the mixture to stand for some time, or I accelerate the operation by heating it to or near to its boiling point until it assumes a rich purple colour, and I then mix it with boiling water and allow the mixture to cool, when cold it is filtered or decanted. The aqueous solution which passes through the filter contains a red colouring matter or dye, while a tarry substance remains on the filter; this tarry substance dissolved in alcohol, methylated spirit, or other suitable spirit furnishes a purple dye. These solutions of colouring matter may be used at once in the process of dye-

ing, concentrated or diluted according to the tints required." It is to be regretted that Dr. Medlock, as a chemist, did not give a more complete and precise description of the method of producing roseine with arsenic acid, for he would then have conferred on this country the honour of having devised the best means of making this important dyeing material. Before giving you the details of the most perfect process of employing arsenic acid in this manufacture, I may here state that the main defect in Dr. Medlock's specification is the insertion of the word 'dry,' in connection with arsenic acid, for with dry (anhydrous) arsenic acid, no colour whatever is obtained, and even when the tri-hydrated or solid acid is used, but a small amount of colour is generated; whilst if a highly concentrated solution of arsenic acid is used, the greatest part of the aniline is converted into magenta. It is mainly owing to this important fact that the following patent of Messrs. De Laire and Girard, dated 26th May, 1860. has proved so successful, and I have great pleasure in laying before you a copious extract from their specification.

"By our new process we put into a distilling apparatus twelve parts arsenic acid, and twelve parts water, and the arsenic acid having become completely hydrated, we add ten parts of kyanol (the "aniline" of French chemists). The whole is then agitated or shaken, so as to produce a thorough mixture, forming a homogeneous, clammy, or nearly solid mass. This mass is heated at a low fire, so as to gradually raise its temperature, when liquefaction takes place. By this *modus operandi* water and only a small quantity of kyanol is evaporated, if the operation is conducted with proper care. At a temperature of 248° Fahrenheit, a great quantity of the kyanol or aniline is already converting into colouring matter, and care should be taken to keep the temperature at that point for some time, after which it is further raised, but in no instance above 320° F. We thus obtain a perfectly homogeneous and fluid mass above 212° F. This operation lasts from four to five hours. When cooled, the mass solidifies and becomes a hard brittle matter, of a coppery hue, similar to Florentine bronze. This matter is highly soluble in water and other solvents, such as alcohol, and imparts them a fine pure, red tint, having no admixture of violet, the intensity of this colouring matter being so great that after having been boiled and concentrated it appears altogether black.

This colouring matter may, without inconvenience, be directly applied to dyeing or otherwise colouring fabrics and other substances, the substance thus coloured not retaining the slightest trace of arsenic. The arsenic may also be eliminated in an easy way by either of the following processes:—

First process. The mass is pulverized and digested with chlorhydric (hydrochloric) or sulphuric acid, diluted with water. The clear solution thus obtained is then saturated with a slight excess of soda or carbonate of soda; thus the colouring matter precipitates, whilst the arsenic is dissolved in the alkali. The colouring matter is next washed once or twice in cold water, when it may be filtered or decanted.

Second process. The colouring matter, after having been dissolved in water is digested with a quantity of lime corresponding with the portion of arsenical compounds contained in it, the lime being slightly in excess. The colouring matter is thus precipitated, as well as the arsenical compounds, which combine into insoluble calcareous salts. The precipitates both, and the solution are then (without being separated) acted upon by either of the carbonic, tartaric, or acetic acids, which dissolve the colouring matter, the whole of the arsenic remaining insoluble.

There are several other means for purifying the colouring matter obtained, such as sulphuretted hydrogen "benzine," any of which agents may be used as may be found most advantageous.

We also obtain a violet colouring matter, and also a combination of blue and other colouring matter, by merely changing the proportions of the arsenic acid used. Thus instead of employing the proportions above stated, if we act with eighteen, twenty, and twenty-four parts of arsenic acid on ten parts of aniline, or a quantity of any salt containing ten parts weight of aniline, a colouring matter is produced that is more or less violet, tending towards the pure blue, and the matter thus obtained may be used directly, as it is, or the blue ingredient may be used as such."

Azalèine, or nitrate of rosaniline, has been extensively manufactured in France under the patent of Mr. Gerber-Keller, and in England under that of Mr. T. D. Perkin. The following is an outline of Mr. Perkin's specification. When aniline, or one of its homologues, is mixed with perfectly dry per-sulphate, per-nitrate, or sub-nitrate of mercury, especially the latter, until no further change of colour or action is produced, the mixture is heated to about 347° F., when the mass becomes brown and gradually changes to a dark crimson, the whole of the metal of the mercurial salt collecting at the bottom of the vessel. The hot liquor is removed from the mercury and allowed to cool, and to purify this solid mass of nitrate of rosaniline, it is simply necessary to wash it first with a little cold water and then to dissolve it in boiling water, from which solution it can be separated in a nearly pure state by the addition of common salt. I will not trouble you with Mr. Gerber-Keller's process, as it is very similar to the above, the principal difference being that this gentleman recommends a temperature not exceeding 212°.

I believe also that a magenta colour was manufactured under a patent of Mr. Greville Williams, by the employment of per-manganate of potash, but as it is merely another method of oxydising aniline, I shall not detain you with further details of the process. Messrs. Dale and Caro also patented, in 1860, a plan for manufacturing magenta, which consists in heating two parts of aniline with two parts of finely powdered nitrate of lead, and carrying the whole to near the boiling point of aniline, viz. 360° Fahrenheit; then one part of anhydrous phosphoric

acid is gradually added to the mass, which is well stirred and maintained at the above temperature for an hour or two. The colour is extracted by hot water, and precipitated from the aqueous solution by common salt, and when dissolved in methylated spirit it is ready for use. These gentlemen have also patented the following process, which is more simple and practical than the above. One part of aniline is saturated with dry hydrochloric acid gas, and this hydrochlorate of aniline is mixed with two parts of dry nitrate of lead, which is added in small portions. The red colour thus produced is treated as described in the previous section of their patent.

Messrs. Laurent and Casthelaz displayed at the Exhibition a fine red colour, said to be produced by a new chemical reaction which, if there is no error in their results, deserves further notice. The novelty consists in obtaining the magenta from nitro-benzine or its homologues without the previous conversion of the same into aniline. To effect this they mixed 12 parts of nitro benzine with 24 parts of iron filings, and six parts of concentrated hydro-chloric acid, which they allow to stand at natural temperature for 24 hours, the resulting solid mass of a resinous appearance is treated with water, which dissolves the colouring matter; and this having been precipitated by chloride of sodium, is again dissolved in water, and reprecipitated by the same agent, when it is considered by the patentees to be *erythro-benzine*, and fit for use; what renders this reaction exceedingly interesting is that it closely resembles that by which aniline is produced, viz. the de-oxydation of nitro-benzine.

I shall complete my observations upon the manufacture of this magnificent colour (magenta) by a short description of a most interesting and novel mode of producing a red colour from aniline, the original idea of which is due to the eminent chemist Dr. Stenhouse, and its realization on a practical scale to Mr. Jules Persoz. On mixing and well agitating together an aqueous solution of furfurol with acetate of aniline, a beautiful red colour is produced, and on being allowed to stand for some time, a red mass is deposited, presenting the brilliant green reflection of cantharides' wings. When the whole of the aniline employed is so transformed, the liquor is removed and the red coloured deposit is washed with water. If it were not for its inability to resist the action of light this colour would compete in brilliancy and beauty with magenta.

The difference between magenta and purple aniline is that when mixed with strong sulphuric acid magenta gives a yellowish solution, whilst purple gives a dark green, but both colours are re-established when large quantities of water are added to the above solutions. Magenta is reduced by sulphurous acid, whilst purple aniline is unaffected by that re-agent. Both give a precipitate with tannin, but I shall refer to the compounds of tannin and colouring matters when I speak of the application of these colours to calico printing. Silk and wool are dyed with magenta, by simply adding some of the colour to a

slightly acidulated bath. The dyeing power of this material is so great that ten grains will dye two square yards of silk.

Blue Colouring Matters from Aniline.

The blue colours from aniline can be classed under three different heads:—

1. Blue colouring matters of light hue, resisting the action of acids, and to a certain extent that of light, but decolorized by alkalies Such are the dye called *Azuline*, prepared by Messrs. Guinon, Marnas, and Bonnet, of Lyons; that prepared under Mr. C. A Girard's patent, and called *Bleu de Lyon*, also *Bleu de Paris*, prepared by the process of Messrs. Persoz, de Luynes, and Salvétat, and probably the *Bleu de Mulhouse*, obtained by the process of Messrs. Gros-Renaud and Schæffer.

2. Blue colouring matters giving shades very similar to those of indigo, offering great resistance to light and alkalies, but turned green by acids. Of this kind are *Azurine*, patented by Messrs. Crace Calvert, Clift, and Lowe, and the same colouring matter as observed by M. Fritzche, M. Emile Kopp, &c.

3. Blue colouring matters of a light shade but highly fugitive, turning yellow when in contact with acids; such as that produced by Mr. Lauth's method.

Although the above classification will enable you to understand the distinctive properties of the various blue dyes from coal tar, it will, in describing the processes by which these colours are obtained, be more convenient to follow another order. I shall, therefore commence by stating, that Mr. Charles Lauth had observed, as early as December 24th, 1860 (see vol. 31 of the Bulletin de la Société industrielle de Mulhouse), that when magenta dyes, but more especially azalèine, were heated with a reducing agent, such as protochloride of tin, a purple and even a blue were obtained. In continuing these researches he also observed that a blue colouring matter could be easily obtained by heating azalèine with various organic compounds, such as aldéhyde, several of the hydrurets, of benzoile, acétyle, and many of the natural essences. But as this blue colour cannot resist the action of acids or light, it is useless to occupy your time with a further description of its manufacture, but the following chemical reaction is worthy of your notice. Mr. Willm has recently published an interesting paper on this aniline blue, which not only shows how aldehyde acts, but exhibits the composition of the blue itself.

Azalèine. Aldehyde. Water.

$$2\,(C_{36}\,H_{20}\,N_4\,O_4) + 5\,C_4\,H_4\,O_2 + 8\,HO$$

Blue or Oxyphenylanilide. Acetate of Ammonia.

$$= 3\,(C_{24}\,H_{11}\,N\,O_2) + 5\,C_4\,H_3\,(N\,H_4)\,O_4$$

Therefore the triamine azalèine has been transformed into a monamine blue, by a new chemical reaction. for aldehyde not only acts as a reducing agent, but converts a part of the nitrogen into ammonia.

Mr. Lauth has also observed a blue colour similar to the above by acting on methylaniline with bichromate of potash. Although the blue I am now about to describe is, like the last, obtained by the reduction of magenta, yet, strange to say, it belongs to the first class, that is, it resists the action of acids, and also to a great extent of light. The process was patented January 12th, 1861, by Mr. C. A Girard, and consists in heating for several hours at a temperature of 329° F., equal weights of magenta and aniline, and allowing the whole to cool; the substance produced is of a violet hue, and is mixed with weak hydrochloric acid, thus removing the excess of aniline and red dye, and leaving a pure purple colour, which is either used as such under the name of *violet imperial* (previously noticed), or further reduced into a blue colour, by boiling it several times with slightly diluted hydrochloric acid, and then washed with boiling water. The substance thus obtained is of a fine blue colour, with a beautiful coppery lustre. To employ this colour in dyeing it is sufficient to dissolve it in acetic acid, or methylated alcohol, and to add these solutions to the dyebeck. I am inclined to think that this colour is the one which was extensively imported into this country under the name of *Bleu de Lyon*, and is now manufactured by Messrs. Simpson, Maule & Nicholson.

There is another similar instance of the reduction of magenta into a purple and blue, and which no doubt is identical in composition with the above, and called *Bleu de Paris*. Messrs. Persoz, de Luynes, and Salvétat, have called public attention to a new blue which they produced, and to which they gave the name of *Bleu de Paris;* this they prepared by heating for thirty hours, in a sealed tube, at a temperature of 356°, one part of anhydrous bichloride of mercury with two parts of aniline. The mass is then treated with boiling water and precipitated by chloride of sodium, this method of purification being repeated several times, until the whole of a green colour is removed. The blue thus produced can resist the action of weak acids and alkalies, but assumes a red hue when acted on by these agents in a concentrated state. Sulphurous acid has no action upon it, and it dyes animal fibres with facility.

But one of the most interesting reductions of aniline red in a commercial point of view is the formation of the *Bleu de Mulhouse*, which is due to Messrs. Gros-Renaud and Schæffer, who operate as follows:— They dissolve in one litre of boiling water

50 grammes of white gum lac,
18 „ of carbonate of soda,
50 „ of a solution of azalèine,

which solution is composed of 125 grammes of azalèine dissolved in half a litre of water, and half a litre of alcohol. The whole is kept boiling for an hour, taking care to maintain the fluid at its original level by the addition of water. A purple colour can also be produced by slightly modifying the above proportions.

But the most valuable and most scientific method of manufacturing aniline blue is that discovered by Mr. Marnas, of the firm of Guinon, Marnas and Bonnet, of Lyons, not only because it is based upon a novel chemical re-action, but also because by it the blue is produced directly from aniline, this substance being gradually and slowly oxydized into a blue, by means of *peonine*, which I shall describe in speaking of rosalic acid. The following is an outline of the patent taken out by this firm. Five parts of peonine are mixed with eight parts of aniline, and the whole heated to the boiling point for some hours, until nearly all the material is transformed into a blue colouring matter, which is purified by successive washings, the first with boiling water acidulated with sulphuric or hydrochloric acids, the second with hot oils of tar, the third with a diluted solution of caustic alkali, and finally with slightly acidulated water. The *azuline* so prepared, presents itself as a reddish powder with a golden lustre, soluble in alcohol, or methylated spirits, which solutions can be used for dyeing or printing. The patentees also claim the right of substituting aniline by naphthalamine, toluidine, cumidine, or other natural or artificial alkaloids.

Azuline.

The following is the process for dyeing silk and wool :—To an acidulated lukewarm bath of water an alcoholic solution of azuline is added, and the silk or wool worked in it until it is of the required shade. It is then transferred to another bath of boiling water, acidulated with sulphuric acid, when the purple colour is dissolved, leaving a most brilliant and permanent blue upon the material. The dyed silk or wool is washed repeatedly, passed through a bath containing a little tartaric acid, and dried.

I shall conclude my observations on this remarkable colour by drawing your attention to the following analysis made of it by Mr. Willm, whose name I have already had the pleasure of citing. He considers azuline to be composed of

$$C_{24}\ H_{12}\ N\ O_4$$

which according to him may be considered as dioxyphenylamide, or

$$N \begin{cases} C_{12}\ H_5\ O_2 \\ C_{12}\ H_5\ O_2 \\ H_2 \end{cases}$$

I shall now proceed to give you an insight into the production of the dark blue aniline colours resembling indigo.

Mr. Fritzche observed, during some of his researches on aniline, the production of a dark blue substance, which he prepared by mixing together equal volumes of a solution of a salt of aniline and alcohol, and adding to this another solution, containing chlorate of potash and hydrochloric acid. After a short time a dark indigo blue precipitate is produced, which when washed with water may be dried and preserved,

but this colour has received no application, owing to the difficulty of dissolving it, either in water, alcohol, ether, oils, hydrocarbons, &c.

Dr. Hofmann also produced this colour hy acting on a solution of hydrochlorate of aniline with a solution of hypochloric acid. Messrs. Clift, Lowe, and myself, also produced it by acting on an acid hydrochlorate of aniline with chlorate of potash, but I shall more especially refer to this process when I speak of its application to calico printing. Mr. Willm has also obtained this peculiar blue by mixing the sesquichloride of iron with nitrate of aniline ; after a short time a chemical action is set up, when the liquor becomes purple, from which is gradually deposited the blue colouring matter. The same reaction is obtained by substituting bichromate of potash for the chloride of iron. This gentleman has also devised another interesting method of procuring this blue, which consists in mixing the same salt of aniline with red prussiate of potash, but the blue produced in this instance is stated to be soluble in alcohol, which is not the case with previous ones.

As these blues resist all chemical agents excepting acids, which turn them green, this is the only drawback to their employment as substitutes for indigo ; but as, notwithstanding this defect, they are employed in calico printing, for producing greens, blues similar to indigo, and such dark blues and greens as to appear black, I shall refer again to these colours when I come to calico printing.

I may conclude my observations on the various processes for producing the aniline colours, by remarking that it is quite evident that magenta may be transformed into purple or blue, and that therefore blue is the first degree of oxydation of aniline, purple the second, and red the third.

Having described different methods of applying the aniline dyes to silk and wool in the course of the preceding observations, it now only remains for me to call your attention to the methods of dyeing vegetable fibres with the same colours, so as to resist the action of soap, as these fibres require a special treatment to adapt them for dyeing, whilst silk and wool, as previously noticed, fix these beautiful colours without the aid of mordaunts. At the last exhibition there were exhibited in the French and Belgian departments some magnificent specimens of cotton yarns, which had been dyed with magenta and purple aniline, after having been prepared as for Turkey red, but that process of preparation is so expensive, that this application of aniline colours does not appear to have been extensively carried out, and, in fact, it has been superseded by the following process devised in 1857, by Messrs. Puller and Perkin. Their process is based upon the formation of an insoluble compound of the colouring matters, with tannin and a metallic base in the fibre. To effect this, the cotton is soaked in a decoction of shumac or any other tanning substance for an hour or two, and then passed into a weak solution of stannate of soda, and after having been worked therein for an hour, it is wrung out and dipped into

dilute sulphuric acid, and well rinsed. To dye the cotton so prepared, it is simply necessary to work it in a slightly acidulated bath, containing purple aniline or magenta.

Cotton may also be dyed a very good and fast colour, by mordanting it with a basic salt of lead, and then working it in a hot solution of soap, to which the colouring matters have been added. Although cotton may be dyed with these colours, by means of albumen or lactarine mordaunts, still there are practical difficulties which have hitherto prevented the adoption of this method.

Several brown colouring matters are produced from aniline by the action of different chemical agents, and as these shades are of secondary importance to dyers, the aim of chemical manufacturers has been rather to avoid, than to promote their production. I have however, lately seen some silk dyed with a brown substance prepared by Messrs. Müller and Co., of Basle, which is probably extracted from some of the refuse products of their manufacture.

Before leaving the aniline colours I will give you an outline of Dr. Hofmann's researches on a yellow colouring matter, called *chrysaniline*, or *phosphine*, which has been discovered by Mr. E. C. Nicholson, and introduced into commerce by the firm of Simpson, Maule and Nicholson. I cannot give you a description of Mr. Nicholson's method of obtaining this colour, because, so far as I am aware, he has not published his process, but from Dr Hofmann's experiments it would appear to be a secondary product, generated during the formation of roseine. Chrysaniline strongly resembles chromate of lead, is slightly soluble in water, and very soluble in alcohol and ether; it is the alcoholic solution which is employed to communicate to silk and wool a beautiful orange yellow colour. Dr. Hofmann has found it to be a well defined organic base, giving with nitric acid a characteristic yellow precipitate, which is very insoluble. The insolubility of this salt has enabled Dr. Hofmann to separate chrysaniline from all other substances, and by boiling it with ammonia, he isolated the base, which he found to have a most interesting relation to rosaniline and leucaniline, as shown by the following diagram.

Chrysaniline	$C_{20}\ H_{17}\ N_3$
Rosaniline	$C_{20}\ H_{19}\ N_3$
Leucaniline	$C_{20}\ H_{21}\ N_3$

As everything relating to aniline is of great interest at the present time, I must not omit to lay before you some recent (January, 1863), researches of Dr. Hofmann's on this important substance. This learned chemist in examining some alkaloids contained in the refuse remaining after the purification of aniline by distillation, and which alkaloids passed over at a temperature of 626° F., succeeded in obtaining two new substances, which he calls respectively *paraniline* ($C_{12}\ H_{14}\ N_2$), (this being in reality two equivalents of aniline condensed into one), and *xenylamine* ($C_{12}\ H_{11}\ N$).

*Opal or Bleu de Lyon.**

*Phosphine.**

*Roseine.**

Colours from Napthaline.

Owing to napthaline (C_{10} H_8) being a refuse product of no value in the manufacture of coal gas, and in the distillation of tar, many attempts have been made to introduce the beautiful colours which it is susceptible of giving when submitted to various chemical reactions; and although these attempts have not hitherto been commercially successful, still the cheapness of the first material, and the great brilliancy of the colours produced, induce me to lay before you a few facts with reference to this subject. Shortly after Laurent had published his remarkable researches on napthaline, Streckner drew the attention of chemists to the great similitude there was between chloroxynapthalic acid (C_{14} H_4 ClO_4), and alizarine (C_{14} H_6 O_4), for he shewed that it was only requisite to replace the chlorine by hydrogen, to transform the acid into alizarine. This acid is yellow, and its salts are orange, yellow, and crimson; silk dyed with the ammoniacal salt acquires a good golden yellow colour, little affected by light. As Mr. W. A Perkin has devoted much time and labour in the endeavour to apply napthaline colours commercially, I cannot do better than give you his own description of the preparation and properties of some of these colours.

"Nitrosonaphthalin.—This peculiar body is a product of the action of nitrous acid on napthaline. It is prepared by mixing a solution of hydrochlorate of naphthaline with nitrate of potassium. From this mixture it separates as a reddish-brown precipitate. This, when washed with water on a filter and then dried, is dissolved in alcohol, filtered, and evaporated to dryness on the water-bath. Thus prepared, it is a crystalline dark-coloured substance, having a greenish metallic reflection. It is soluble in alcohol and also in benzole, forming orange-red solutions.

When acids are added to an alcoholic solution of nitrosonaphthalin, it immediately assumes a most beautiful purple or violet colour as fine as any of the aniline purples. Alkalies restore it to its original colour. Silk may be dyed a beautiful purple shade with this substance, provided a certain quantity of hydrochloric or sulphuric acid be present; but what is most unfortunate is, that when the silk thus dyed is rinsed in water, the colour immediately passes back to that of pure nitrosonaphthalin, and, also, that the amount of acid required to keep up the purple shade, if left in the silk, rots it in a few days. Could this purple be fixed, nitrosonaphthalin would become a cheap and most useful dye.

* Kindly supplied by Messrs. E. Brooke and Co.

I have endeavoured to produce a sulpho-acid of nitrosonaphthalin, thinking that if such a compound could be obtained, it would possess the purple colour, because it would be an acid itself. But although sulphuric acid does dissolve it, forming a blue solution, no combination takes place. I also endeavoured to produce this desired result by treating sulphonaphthalamic acid with nitrous acid, but obtained only nitrosonaphthalin, the acid of the sulphonaphthalamic acid having apparently separated.

NAPHTHAMEIN.—Piria observed that naphthalamine and its salts produce blue precipitates, afterwards becoming purple, when brought in contact with perchloride of iron, terchloride of gold, nitrate of silver, and other oxidizing agents. This product of oxidation he terms naphthamein. Silk and cotton may be dyed with it; but the colour of this compound is so inferior as to render it useless as a dyeing agent."

Naphthalamine.—This substance, which has the same relation to naphthaline, as aniline has to benzine, is obtained by a series of chemical transformations similar to those which benzine undergoes in order to be converted into aniline, and has been recently manufactured on a rather extensive scale by the Tower Chemical Company near Manchester, Naphthalamine crystallizes in white needles, is fusible at 86°, boils at 572°, is nearly insoluble in water, freely soluble in alcohol and ether, and combines readily with acids. This product of naphthaline appears to me to be the one most likely to yield colours susceptible of application in dyeing and calico printing, for it assumes under the influence of various oxydising agents, similar colourations to those presented by aniline when acted upon by the same agents. Thus, Mr. Brunner produced in my laboratory, about three years ago, a very fine purple, by heating at a moderate temperature, a mixture of naphthalamine and arsenic acid, which after proper purification, imparted very satisfactory colours to samples of silk, and animalized cotton. Mr. du Wildes published about the same period, a method of producing a purple with naphthalamine, which consisted in heating a mixture of this alkaloid with the nitrates of mercury.

Mr. Roussin has also published an interesting paper on this subject, and finds that if a colourless solution of hydrochlorate of naphthalamine is mixed with a solution of nitrite of potash, a fine red precipitate is produced, which is completely insoluble in water. The formation of this colour on fibres is most simple and easy, for if skeins of silk or wool are first dipped in a solution of hydrochlorate of naphthalamine, and after having been wrung are then plunged into a solution of nitrite of potash, washed and dipped in a weak alkaline bath, the fibres acquire various shades of red or maroon, according to the more or less diluted state of the liquor. What especially characterizes this colouring matter, is its resistance to the action of light, of acids, of alkalies, and lastly of chlorine. Mr. Roussin has further observed the production of a violet red colour of great intensity, by acting on naphthalamine in the same manner as Messrs. Persoz, de Luynes, and Salvétat, acted on aniline to produce a purple and a blue already noticed. Thus on heating to a temperature of 472°, a mixture of hydrochlorate of naphthalamine and

protochloride of tin, a blackish brilliant mass is obtained, which on being well washed with water, yields to alcohol a fine red purple colour. Mr. Roussin further adds that when this colour is applied to fabrics it resists the action of light, acids, and alkalies.

Lastly, Messrs. Guinon, Marnas, and Bonnet, also propose to employ naphthalamine as a substitute for aniline in the production of a blue colour, for which purpose large quantities of the compound have been commercially prepared.

Carbolic Acid.

This product of coal tar is destined to play a most important part in the production of artificial colours, for it has already yielded in the able hands of Mr. Marnas three valuable dyes, viz. :—a blue dye (*azuline*) already noticed, a red dye (*peonine*), and a yellow dye (*picric acia*), both of which I shall presently describe.

Carbolic Acid, (C_{12} H_6 O_2), which was discovered by Runge, is now prepared by a process devised by Laurent; it consists in treating the oils of tar which boil between the temperature of 300° or 400°, with a highly concentrated solution of hydrate of potash or soda, when a white crystalline substance is formed and precipitates. The supernatant liquor is decanted, and the solid mass dissolved in a small quantity of water, the whole separating into two layers, the lighter, or oily-like mixture of acid substances being removed, and hydrochloric acid added to the other, or aqueous portion, which separates the carbolic acid as an oily substance floating on the surface of the saline fluid. The carbolic acid is further purified by washing and distillation. Carbolic acid presents itself in long colourless needles, melting at a temperature of 96°, and boiling at a temperature of 370°. It is soluble in 25 parts of water, and freely soluble in alcohol, ether, and concentrated acetic acid. Carbolic acid when heated with ammonia in a sealed tube is partially converted into water and aniline, and the same result follows when vapours of carbolic acid and water are passed over heated cyanide of potassium. If a piece of pinewood is dipped in carbolic acid and then in hydrochloric acid, and afterwards allowed to dry in the atmosphere, it assumes a beautiful blue colour. Another characteristic property of this substance has been lately published by Mr. Berthelot, consisting in giving a beautiful blue colour when it is mixed with a little ammonia and chloride of lime. Mr. Monnet has observed that carbolic acid combines freely with two equivalents of sulphuric acid, forming a compound called sulpho-carbolic acid, which compound gives even when much diluted with water a fine purple colour, on being mixed with perchloride of iron. This same compound also assumes various colours when brought into contact with binoxide of nitrogen. But the most interesting property of carbolic acid is its conversion by means of oxydation into a red colouring matter, called rosalic acid.

Rosalic Acid.—This beautiful red colouring matter was first discovered by Runge, in 1834, who remarked its production as well as that of red-

brown colour, called *brunalic acid*, whilst examining some refuse products of carbolic acid. Runge succeeded in separating rosalic acid from brunalic, by dissolving them in alcohol, and adding a solution of lime, which precipitated the brunalic acid, and left in solution a rosalate of lime, from which the rosalic acid was separated in the form of a dark red precipitate on the addition of acetic acid. In 1857, Mr. Tschelnitz observed that when the oils of tar or carbolic acid were left in contact with the atmosphere and lime, the latter became red, which coloration he ascertained was due to the formation of rosolate of lime. Dr. Hugo Müller also noticed that when crude carbolate of lime is exposed to a moist heated atmosphere, as that of an ordinary drying stove, it gradually assumes a dark red tint, rosolate and brunalate of lime being formed. After having separated rosalic acid by the process first adopted by Runge, and further purified it, Mr. Müller states that pure rosalic acid is a solid substance of a dark red colour, with the green lustre of cantharides, insoluble in water, soluble in alcohol, ether, alkalies and alkaline earth solutions, communicating to these a most magnificent crimson colour, which I regret to say is altered by light. But we owe to Dr. R. Angus Smith the explanation of the transformation which carbolic acid undergoes to become rosalic, which consists in the fact that two equivalents of carbolic acid, by absorbing two equivalents of oxygen become transformed into one of rosalic.

$$\underset{\text{carbonic acid.}}{2\,(C_{12}\,H_6\,O_2)} + 2\,O = \underset{\text{rosalic acid.}}{C_{24}\,H_{12}\,O_6}$$

He arrived at this result by passing vapours of carbolic acid over a heated mixture of caustic soda and peroxide of manganese, the peroxide of manganese yielding oxygen to the carbolic acid, and the rosalic acid thus formed combining with the soda. The rosalate of soda on being dissolved in water readily yields rosalic acid on the addition to it of acetic acid. Mr. Jourdain, in a paper recently published, confirms Dr. Smith's results, and gives a more active means of oxydising carbolic acid by passing vapour of carbolic acid, at a temperature of 302° over a mixture of binoxide of mercury and soda, when metallic mercury and rosalate of soda are the results of the reaction. On dissolving the mass in water, mercury deposits at the bottom of the vessel, and pure rosolate of soda remains in solution.

But the most interesting method of producing this colour has lately been published in a patent taken out in this country by Messrs. Guinon, Marnas and Bonnet, who proceed as follows:

"Take about twenty-three pounds of phenic or carbolic acid, from about ten to twenty pounds of oxalic acid, and from about seven to fourteen pounds of sulphuric acid. This mixture is heated until the colouring matter is formed of the requisite color and consistence. When this operation is considered to be finished, the matter is washed with boiling water, in order to remove the excess of acid. It is then in the state of a light pitch, and with a green shade of cantharide. It may be dried and reduced to powder by means of heat, or by a longer process without heat."

Peonine.—Up to a very recent date, no means had been discovered of fixing this splendid colour (Rosalic acid) on fabrics, nor of modifying it so as to render it fast. This important result has, however, been attained by a most ingenious process, and one which will ultimately prove extremely valuable in the art of manufacturing artificial colours, for the above-named gentlemen have proved that the loose colours rosalic acid and rosalate of ammonia can be rendered fast, if rosalic acid and ammonia (or rosalate of ammonia) are heated together to a sufficient temperature so that the elements may react one upon the other, to produce water and amide, or in other terms, so as to incorporate nitrogen as one of the elements of the compound resulting from the reaction. What renders this reaction (or the formation of Peonine) still more interesting is, that by the introduction of nitrogen to the colour itself, it imparts to it the property of fixation upon fabrics which do not contain that element, and thus places those fabrics more nearly on a par in this respect with those which, as is well known, owe their power of receiving dyes to the presence of nitrogen in their composition; for example, wool and silk as compared with cotton and linen. This discovery is sufficiently important to justify me in giving you *verbatim* the specification of Messrs. Guinon, Marnas and Bonnet.

"The matter thus produced is converted into more solid matter by the following process. Take about two pounds and a quarter of this less solid matter, and about five pounds and a half of ammonia of commerce. This mixture is put into a closed metallic vessel, then heated to a temperature of about 270° of Fahrenheit for about three hours. This is allowed to cool, and then the vessel is opened. The matter originally introduced therein becomes completely dissolved in the ammonia, thence yielding a liquor rather thick, and possessed of a considerable colouring power. This liquor when treated by acids furnishes a deep red precipitate, which is the fast colouring matter modified as required, and which is capable of dyeing red silk, wool, and other textile materials.

"The matter thus prepared is called 'Pèonine,' and is applicable to dyeing and printing generally.

"Having thus described the nature of the said invention, and in what manner the same is to be performed, I would remark that in the first part of the process or processes hereinbefore described, other oxydising bases may be employed, such as salts of mercury or other salts, arsenic acid, oxide of lead, and others, not only on ordinary phenic or carbolic acid, but on the analogous substances such as creosote, 'cresil,' and others. And in the second part of the process or processes hereinbefore described ammoniacal salts or other azotic bases such as the acetate or benzoate of ammonia, urea, and others, used at a suitable temperature, either with or without pressure. But what I claim as of the invention communicated to me from abroad as aforesaid is, the preparation of a red colouring matter from phenic or carbolic acid as hereinbefore described, and the application of the same to dyeing and printing."

Picric or Carboazotic Acid. This acid, which has been known to chemists for many years, was formerly obtained by acting with nitric

acid on a variety of organic substances, such as indigo, benzoin resin, xanthorrhea hastilis, salicine, &c.; the use of these substances was however superseded by that of the oils of tar boiling between 300° and 400°, and finally by carbolic acid; this last process having been discovered by Laurent, and first carried out commercially by myself.

When nitric acid acts upon carbolic acid it gives rise to three successive degrees of oxydation, viz.:—

Mononitrophenic C_{12} H_5 (N O_4) O_2
Binitrophenic ... C_{12} H_4 2 (N O_4) O_2
Trinitrophenic... C_{12} H_3 3 (N O_4) O_2

the composition of carbolic acid being C_{12} H_6 O_2, consequently the above products are generated by the substitution of hyponitric acid for hydrogen, and as the first two are only interesting in a scientific point of view, I shall confine my remarks to the third, viz.—trinitrophenic or picric acid.

The process for manufacturing picric acid consists in acting upon carbolic with nitric acid, when a violent action ensues, and the above mentioned products are obtained, but by continuing the chemical action, the first two are transformed into the third or trinitrophenic acid. The whole being allowed to cool, fine crystals of picric acid are deposited, which can be further purified by dissolving the acid in water, neutralizing it with carbonate of soda, crystallizing this salt, and obtaining the acid from it, by decomposing the hot solution of the salt with a slight excess of sulphuric acid, when pure picric acid will deposit in the form of elongated rectangular blades, of a very pale yellow colour. These crystals have an intensely bitter taste, which is communicated to the various salts which arise from its combination with metallic oxides. Most of these salts when heated, are of a highly fulminating or explosive nature. Picric acid has the curious property (lately observed by Fritsche), of combining with several hydrocarbons, and forming insoluble crystalline compounds. It possesses very extraordinary dyeing powers, one part of acid being sufficient to give a tinge to 300,000 parts of water. All animal fibres are dyed by it with great facility, and when pure, and carefully prepared, it communicates to them rapidly, without any mordaunt, a most brilliant yellow colour, the fastness of which will be found commensurate with the purity of the dye. M. Emile Kopp states, that one part of pure picric acid dissolved in water, with a little sulphuric acid, is sufficient to give to 1,000 times its weight of silk a moderate shade of yellow. Although picric acid will dye wool a fine shade without any mordaunt, still if the wool is first mordaunted with a little cream of tartar and alum the colour is much faster. Animal fibres so dyed resist satisfactorily the action of light and air. This colour gives with refined extract of indigo or prussian blue most magnificent greens, as already mentioned.

I shall now proceed to mention some of the transformations which this acid undergoes, resulting in the production of two different colouring matters.

Picramic Acid.—Wöhler was the first to observe that when picric acid was reduced by a hot solution of sulphate of protoxide of iron, and caustic baryta was added, a beautiful red salt crystallized as the liquid was allowed to cool, from which he isolated an acid which he named *nitrohematic*, and now called picramic. Mr. A. Girard has given us the best process for obtaining this acid. It consists in reducing picric acid by sulphurretted hydrogen, as shown by this formula.

$$C_{12}\ H_3\ 3\ (NO_4)\ O_2 + 6\ HS = C_{12}\ H_3\ 2\ (NO_4)\ (NH_2)\ O_2 + 4\ HO + 6\ S.$$

The picramic acid obtained by this process presents itself in the form of needles of a brilliant ruby red, freely soluble in alcohol and ether, and but slightly so in water.

Isopurpuric Acid.—This interesting transformation of picric acid, would, if it had been discovered a few years sooner, have possessed considerable importance, for it would have been a cheap method of producing murexide, a dye at one time very extensively used. Mr. Carey Lea first observed that cyanide of potassium had a marked action upon picric acid, but it was Mr. Hlasiwetz who first fully investigated the subject, and devised the following method of producing the remarkable acid, *isopurpuric*. To an aqueous solution consisting of two parts of cyanide of potassium to four of water, at a temperature of 140°, is added slowly, one part of picric acid dissolved in nine parts of boiling water. The liquors acquire an odour of ammonia and cyanhydric acid, and on cooling, yield an abundant crystalline mass. The whole is thrown on a filter, and the solid mass washed with a little cold water; it is then dissolved in boiling water, from which well defined crystals of isopurpurate of potash are deposited, which have a red brown colour with transmitted light, and a green metallic one with reflected. By substituting ammonia for potash *isopurpurate of ammonia* is formed, which is isomeric with purpurate of ammonia or murexide. I believe, with Mr. Nickles, that if cyanide of ammonium were substituted for cyanide of potassium, or still better if the salt of potash above mentioned were decomposed by chloride of ammonium, murexide would be forthwith obtained.

MISCELLANEOUS BLUE COLOURING MATTERS.

Cyanine.—M. Menier exhibited in the French court of the last exhibition, fine crystals, the faces of which glistened with a metallic green lustre, having a golden reflection, and which represented cyanine in a great state of purity. These crystals are nearly insoluble in ether and water, but freely soluble in alcohol, and the latter solution is of a deep blue colour with a coppery lustre on its surface. The colour is destroyed by acids and ammonia, and alkalies precipitate it from its alcoholic solutions. The green crystals are the iodide of a peculiar alkaloid which is

isomeric with iodide of amyl-lepidylammonium, and have the following composition :—

$$C_{60}\ H_{39}\ N_2\ I$$

or two equivalents of amyl-lepidine, minus one equivalent of hydroiodic acid. Dr. Hofmann, to whom we owe our knowledge of the composition of this beautiful blue colour, detected with great skill that this substance was soiled with a small quantity of the iodide of amyl-chinoline ammonium. The magnificent blue solution which cyanine yields when dissolved in alcohol attracted so much attention at the time of its discovery by Mr. C. Greville Williams, and by the subsequent offer from the Société Industrielle de Mulhouse, of 10,000 francs for its fixation, that I deem it my duty to give you an outline of the process by which it is obtained. When cinchonine is distilled with caustic potash a large quantity of various volatile alkaloids distil, among which are lepidine and chinoline. In order to procure the blue colour with this product, one part of impure lepidine is boiled for ten minutes with one and a-half parts of iodide of amyl. After allowing the mass to cool, it is boiled for a short time with six parts of water, and the whole being thrown on a filter, the liquor is carried to the boil, and a solution of caustic potash gradually added, when the fluid is again filtered to separate some resinous substances. The resulting product is a solution of the magnificent blue colour cyanine, with little or no shade of red. The high favour which this colour first obtained has not been contiuued, owing to its being fugitive.

Blue Colour from Cotton Seed Oil.—Mr. Kublmann studied in 1861 the production of a blue colour from this novel and unexpected source of production, but as it has received no application, I shall only say a few words upon it. When the refuse which remains from the refining of cotton seed oil is maintained for six hours, at a temperature of 212° with 3 or 4 per cent of concentrated sulphuric acid, 48 per cent of their bulk is converted into a dark blue colouring matter. To separate this from the other substances existing in the mass, it is repeatedly washed with warm water, and acted upon with boiling alcohol, which dissolves the blue colour ; this can then be separated in a solid form by the addition of water. To obtain it quite pure it is washed when dry with benzine.

THIRD LECTURE.

Calico Printing.

The art of calico printing depends upon so many branches of mechanical as well as of chemical science, that it is impossible for me to give detailed information of all the improvements which every department of this manufacture has undergone, during the period embraced by this course of lectures. I shall, however, draw your attention to a few of the prominent points that have come under my notice, but before doing so allow me to make a few observations on the late Exhibition. It is to be regretted that many important firms of various countries, but especially of Great Britain, declined to take part in the recent Exhibition. From this remark, however, must be excepted France, who omitted nothing requisite to insure a worthy display of her excellence in this branch of manufacture, whether by encouraging the competition of the various houses, or by a judicious and systematic selection of those most likely to sustain her credit. Notwithstanding the above-mentioned grave disadvantage, the printers of the United Kingdom have made since the Exhibition of 1851 most important advances in this branch of manufacture. Thus in the recent Exhibition the printers of Great Britain, though comparatively few, have shown by many examples that they are well able to avail themselves of the mechanical and chemical means at their disposal for producing a large variety of goods fitted, both by design and execution, for this as well as for numerous foreign markets; and there can be little doubt that the close observer of the goods exhibited, even by a few only of our best printers, will form the opinion that no country surpasses, if it equals, Great Britain in the class of goods called "cheap and fast prints," which class, after all, forms the great staple of our production. It should be kept in mind, in estimating the comparative merits of different styles of printing, that the great aim of the British manufacturer is to find cheap methods of producing, in large quantities, good, but at the same time low-priced prints; for some of our printers will turn out as many as a million or a million and a half of pieces in a single year. It follows, therefore, that the printers of Great Britain, as well as those of several other countries, are obliged to cultivate both precision and rapidity of

execution, impossible of attainment with methods which may well remunerate the foreigner who aims at extreme delicacy and finish of workmanship, but whose interest, at the same time, is to produce only in limited quantity. For instance, several of the leading French houses exhibit goods which, at a short distance, appear like embroidery, instead of, as they are, merely prints; this effect is obtained by pasting the entire piece on a long table or frame, and then skilfully applying the colour with blocks. When the piece has been removed, washed, and finished, the colours have a body, and at the same time, through not having penetrated the substance of the cloth, they acquire a transparency which produces on the eye an effect as if the pattern were in relievo. Fine examples of this style of printing were to be seen in the cases of Guillaume and Son and Onfroy and Co. The chief difference, however, between this Exhibition and those of 1851 and 1855, is the extension of the pigment style; for whereas in 1851 the class of goods produced in that style was extremely limited, in 1862 they formed the greatest bulk of the prints exhibited, and, by their brilliancy of colour and beauty of design, obtained the admiration of the jurors and the public in general. Although no one could otherwise than admire these beautiful specimens of human skill (especially in the French department) which rivalled in form and colour the productions of nature, still every well wisher of the art of calico printing must regret that this style should have so entirely eclipsed the more permanent though less brilliant style which supplies the wants of the million, and which was so beautifully exemplified by the goods shown in the British department; as for example the fabrics exhibited by Messrs. T. Hoyle and Sons, Butterworth and Brooks, Littlewood and Wilson, Bradshaw and Hammond, Macnaughton and Thom, Newton Bank Printing Company, &c. Let me also state that there were in the class with which I was connected 196 exhibitors, of whom only 59 were British, and that the following remarks were suggested to my mind in examining the goods of various countries.

Austria never appeared to equal advantage in any previous Exhibition; the designs were varied and in good taste, and the quality of colour and neatness of impression were alike excellent.

Though the *Zollverein* showed no printed calico, there was a good collection of printed silk handkerchiefs, and a fine collection of cheap printed shawls and carpets from *Saxony*.

Russia displayed, as already noticed, some good specimens of Turkey-red dyeing, especially those obtained with the species of madder known by the name of *Marena;* also a good collection of goods well suited for Eastern markets, especially in the style called *Lapis*.

It is to be regretted that the best printers of *Belgium* and *Switzerland*, like those of Great Britain and the Zollverein, abstained from exhibiting, and it is therefore impossible to form a correct idea of the progress of calico printing in those countries.

It may be as well to state here, though there were no prints of native production in the Indian Department worth notice, the COTTON SUPPLY ASSOCIATION exhibited, through Mr. Cheetham, some fine specimens of goods printed in England on Surat cotton; and although the details of the processes used are not sufficiently known for a close comparison of these goods with similar ones printed on American cotton, still the results were so good as to be highly satisfactory, and warrant the belief that Surat cotton may be very eztensively substituted for American.

FRANCE.—What has been already said will doubtless have led to the anticipation that the printed goods exhibited in the French department were, generally speaking, of a very high class, and justified the reputation which the best printers of France have long since acquired, especially in those fashionable styles known popularly by the name of *haute nouveauté*. In this class of prints elegance of design, beauty of colour, and delicacy of execution stood unrivalled by those of any other nation, and they applied the new tar colours with a perfection of skill which left nothing to be desired. It will also be seen in the course of this report that they exhibited several original improvements.

Engraving of Rollers.—This branch of calico printing has made great progress. Not only have the engravings acquired sharper outlines and finer details, but the methods of engraving have greatly multiplied. I may cite as instances the application of the principle of the pentagraph, so as to trace patterns on the surface of copper rollers, by Messrs. Smith, who as well as Messrs. Lockett, Sons, and Leake, have effected such improvement since the first pentagraph was exhibited in 1855, as to render this mode of engraving most useful to the art of calico printing. Calico printers have also extensively availed themselves of Mr. Lockett's improvements for producing the groundwork of prints, or as they are termed "covers," by applying "eccentric engraving," or etching, which produces with facility most complicated patterns on a varnished roller, by means of a diamond point guided by machinery. Another improvement, highly interesting in a scientific point of view, is the application of galvanism to the diamond tracer, by Mr. Gaeff, of Paris, which is doubtless destined to exercise considerable influence upon the progress of calico printing. By combining the galvanic action with an eccentric motion, most beautiful and delicate engravings may be produced. This is done by tracing the pattern with varnish on a zinc cylinder, which is so placed in the engraving machine that as a needle passes over its surface and comes into contact with the zinc, the galvanic current is established, and by simple machinery causes the diamond to trace the corresponding pattern on the copper roller. The communication is so rapid and precise that a great saving of time is effected. In the last exhibition, there were two machines in which this was very successfully applied, several diamond points being made to engrave at the same time the same patterns on

various parts of the copper roller. But if mechanical art has greatly assisted the engraver, chemistry has rendered him equally important services, by enabling him to abandon costly and cumbrous modes of impressing by force the designs on the cylinder, substituting for them a great number of etching processes. By some of these processes, as by every other addition to the resources of the engraver, an entirely new and beautiful class of engraving is produced, unattainable by any other known means. For instance, owing to various improvements, rollers of 43 inches in circumference and 44 inches long have been introduced, enabling the calico printer to produce cheaply large furniture patterns.

En passant, I wish to call your attention to an application which has been made of a process greatly admired by many of you at the Exhibition of 1851, invented by Mr. John Mercer, the eminent calico printer, by which the beauty of dyed and printed goods was increased by passing the cotton fabrics through a strong solution of caustic lye, and afterwards through a weak solution of sulphuric acid, and then thoroughly washing. If this process has not been generally adopted, it is no doubt owing to the contraction which the cotton fibres experience under the above chemical influences, but the increased strength which the fibre thus acquires has been turned to good account, by enabling the printer to use it as a substitute for what is technically called the "blanket," that is, an endless cloth which passes over the engraved rollers with the goods to be printed. This material is found by its strength to resist better than most others the heavy strain which the blankets have to undergo during printing.

Bleaching.—One of the main improvements in bleaching calicoes has been that of effecting the operation under high-pressure, which by facilitating the conversion of insoluble matters into soluble ones, simplifies and quickens the process. The method of Mr. Barlow and others, of forcing the scouring liquor to circulate uniformly through the cloth by means of pressure, causes much more speedy and regular removal of the impurities of the material. Great improvements are stated to have been effected on the continent in the bleaching of grey calicoes, by the following process, by which the pieces, instead of being dipped in cold water, as they usually are on their arrival at the bleacher's, are soaked in water at a temperature of 140°, to which a small quantity of malt is added; this causes the conversion of the starch in the pieces into dextrine or sugar, thus facilitating greatly the removal of the size from the warps.

Singeing.—I shall here also allude to two improvements effected by Mr. John Thom, of Manchester. The first, applicable to all kinds of cotton or woollen fabrics, destined for printing or dyeing, consists in an improvement in the singeing or removing the nap from fabrics. The usual mode is to pass the fabrics either through a gas flame, or over a semi-circular heated iron plate. In the latter case, however, a large

amount of fuel was wasted in maintaining the heat of the plate, owing to the free radiation of heat into the atmosphere, and to its absorption in the currents of cold air in contact with the plate. Mr. Thom's invention remedies these defects, by enclosing the plate under a brick arch, so that no air can enter the chamber except that which passes with the piece, and that limited quantity is, by a proper arrangement of flues, conducted into the furnace which heats the plate.

Messrs. Joshua Schofield and Sons have introduced a new machine, for singeing with gas, patented by Mr. James Cooke, which ingenious mode of singeing differs from the old method, in that instead of the gas flame being drawn through the fabric it is made to flow upon the surface, thereby removing the nap without destroying the loose fibres in the interstices. In consequence of the great heat of the flame, which is a mixture of coal gas and oxygen, the goods can be passed over with such rapidity as to remove the nap without injuring the fabric, a great advantage for fustians and heavy goods. To give an idea of the rapidity and consequent economy of this process, it is stated, that at Messrs. Edmund Potter and Co.'s works, more than 4000 pieces of calico have been singed in a day with this machine. Lastly, this machine, which consumes only 1000 feet of gas for 1000 pieces, has the same advantage as that of Mr. Thom, viz.: that it does not allow the fumes from singeing to create any offensive odour.

Sulphuring.—The second improvement of Mr. Thom was devised some years ago, but it is only recently that it has come into general use amongst printers. It is especially applicable to mixed fabrics, such as *mousselines-delaine*, which require, after they have been singed and before they are printed, to be bleached. This was formerly effected by hanging, for several hours, the moist pieces in chambers filled with sulphurous fumes, and is now performed by Mr. Thom's process in a few minutes, by passing them over a number of rollers confined in a chamber filled with the same vapours.

Printing Machines.—Although of late years many improvements have taken place in the construction of printing machines, most of which are of too technical a nature to be described in this lecture, still there are one or two which have exercised so marked an influence on the general progress of the art of calico printing as to require notice. One of these is the arrangement by which an independent motive power is provided for each machine instead of connecting all machines in an establishment with one steam engine; the advantage thus gained by the machine printer is to regulate the speed of his work at any moment; at the same time the spent steam is made to pass into the drying machines, thus affecting an economy and drying the pieces more quickly. Another improvement is the greatly increased number of rollers which each machine is adapted to work; thus there are some Lancashire houses which can print from 16 to 20 colours simultaneously. Messrs. Onfroy and Co., of Paris, exhibited at the last

Exhibition a most ingenious means of obtaining reserves on fabrics, which improvement is the more advantageous, the chemical reserves generally in use being imperfect in their composition, of difficult application to the fabric, and still more difficult of removal. The ingenious process of Messrs. Onfroy consists in punching out patterns from a sheet of cardboard lined with gutta percha, in such places as are intended to remain white or reserved. The cardboard is then rolled on the pressing cylinder of the printing machine, so that when the machine is working, the parts of the pattern which have been cut out receive no impression, and thus form the reserve parts of the pattern. It is evident that to obtain satisfactory results the greatest precision must be observed in applying the cardboard to the pressing cylinder, so that the engraving roller will only apply where required. The great advantage of this mode of producing reserves is that by employing a pressing roller of sufficient diameter, reserves of large surface can be easily obtained. This same firm also exhibited a machine called *Tireur mecanique*, which is a great improvement on the old Tobby sieve, or the other mechanical means which have been devised to enable the block-printer to carry on his block several colours at once. M. Onfroy has succeeded in enabling the block-printer, by simply moving his feet, to feed the surface of his sieve with a great variety of colours, and to level them with a brush, also mechanically moved, so that whilst he is applying the block to the fabric the machine is preparing the colour for feeding it afresh.

Thickening Substances.—It will be readily understood that it is necessary that the mordants or colours to be printed, should be of sufficient consistency to remain on those parts of the fabrics when they are left by the rollers, so as to produce sharply-defined patterns, and as a great variety of chemical products are employed, a great variety of thickeners becomes also necessary.

Thickeners can be classed under two heads. Firstly, those which are merely employed to give proper consistency to the colouring matters, and secondly, those which not only fulfil that purpose, but also serve to fix the colours on the cloth. As I intend to refer to the second class when speaking of the pigment style of printing, I shall here confine my remarks to the first class of thickening substances. I may, however, just state that egg albumen is obtained by evaporating in the air at a moderate temperature the white of eggs; blood albumen by heating in the same manner the serum of blood separated from the red colouring matter called hematosin; lactarine by curding milk with an acid or rennet, collecting the curd caseine, and washing and drying it; and gluten by making wheaten flour into a thick dough, aud washing the same under a gentle stream of water, which removes the starch and leaves the elastic substance called gluten. The first class of thickeners consists of wheaten flour, wheaten starch, farina, sago, gum arabic, gum senegal, &c., and also of a variety of artificial

gums or preparations of flour and starch, which were called into use in consequence of the great increase in the price of gum arabic arising from its extensive employment in printing. Thus farina heated to a temperature of 250 to 300°, and thereby rendered soluble as a gum, became extensively employed as a substitute, and of late years it has assumed an important place in the list of materials used by calico printers. To effect this curious change at the present day, farina is heated to the above temperature, either in a revolving cylinder or in iron troughs placed in a stove for several hours, when it acquires an umber colour, and becomes soluble in water. This change is entirely a molecular one, as the raw and calcined farina have the same composition, notwithstanding which, farina gives a blue colour with iodine, and when calcined a purple. As the colour of calcined farina is an objection to its employment in many instances, it was a great desideratum to find a process for its conversion at such a low temperature as to leave the converted farina nearly colourless. This was first effected in 1838, by M. Payen, who found that if to 400 parts of dry farina one part of nitric acid at 1·40 was added, after having been diluted with sufficient water to form with the farina a hard paste, and this then dried slowly and heated in a close chamber for 20 hours, at a temperature of 200° a nearly white farina was obtained. It is interesting to observe how so small a quantity as a few thousandths of acid can effect this great molecular change. Since that time many processes have been devised to attain the same end, for instance the employment of lactic acid by Mr. Edward Hunt, of oxalic and tartaric acids by others, and lastly a process by Mr. Charles O'Neil, which is valuable as it enables him to convert insoluble farina into soluble farina, or *dextrine*, without any change of colour. This he effects by subjecting starch, farina, and other amylaceous substances to the chemical action of muriatic acid gas, or other acid gas or vapour in a cylinder, the exterior of which is surrounded by an atmosphere of steam. This beautiful preparation has extended the employment of soluble farina as a substitute for gum arabic, the colour which was inseparable from farina previous to this discovery excluding its use in many instances. As calico printing in its present extraordinary development requires thousands of tons of soluble materials for thickening the mordants and colours used, a great variety of this class of artificial gums are prepared so as to meet these requirements. Thus, besides farina, sago, rice, slimes and wheaten flour are used; the latter when heated generally bears the name of British gum, which differs from calcined farina in being soluble in water only at a boiling temperature.

Madder Styles.—Although there has been no marked change in this important branch of calico printing, still there are one or two departments in which considerable improvements have been effected, to which I desire to draw your attention, and to enable you better to understand the nature of these improvements, I shall describe them

in the order in which they come into play in the production of this class of goods. The first is the improvements in patterns, arising out of the before-mentioned advances in the art of engraving. Secondly, a saving in the quantity of mordant used; for the fact which I have already stated with reference to commercial alizarine, viz., that weaker mordants are required, has been proved by Mr. Pincoffs to hold good with all the other preparations of madder, the strength of the mordant required to obtain the same intensity of shade being less, in proportion as the colouring matter is purer. It is also advisable that I should here state that the mordants generally used for madder styles, are the pyrolignites, or acetates of iron and alumina, which under the influence of "ageing," to be described presently, are so decomposed or modified as to leave on the cloth, either an insoluble oxide or a subsalt, which becomes the intermediate agent for fixing on the fabric the colouring matters called alizarine and purpurine, iron giving from a dark purple to a light lilac, alumina from a dark red to a pink, and a mixture of these two mordants a variety of chocolate tints. Thirdly, the most important improvement which has taken place in this branch of printing, viz., a great saving of time and labour in the fixing of mordants by ageing, was first practically carried out by Mr. Walter Crum, the eminent scientific calico printer. Dr. Schunck says that, "On the proper ageing of printed goods depends, in a great measure, the success of many styles; should a room be too hot or too dry, imperfect fixation of the colour ensues, and meagre and uneven tints are obtained in the subsequent operations.

To give a further idea of the importance of this step in calico-printing, I may state that 'ageing-rooms' as they are called, are in several print works of enormous dimensions, and are generally a separate building. Those of Messrs Edmund Potter and Co., and Messrs. Thos Hoyle & Sons, may be particularised as forming quite a feature in their works. The process of ageing in calico printing is that by which a mordant, after being applied to a cotton fabric, is placed in circumstances favourable to its being completely incorporated with, and fixed in the fibre. It has generally been found desirable that calico printed with a mordant, should, before dyeing, be exposed to the atmosphere for some time in the ageing-room in single folds, which, generally speaking, requires several days, the object being, as before stated, to liberate the acetic acid from the acetates of iron or sulpho-acetate of alumina, and to oxydise the protoxide of iron. It was for many years believed that oxygen was the only necessary agent, and although some printers had observed that moisture facilitated the process, this fact was not generally known until Mr. John Thom, of Manchester, claimed the introduction of moisture as an important agent in the phenomena of ageing, in a patent which he took out in 1849. Mr. Walter Crum, F.R.S., was the first printer, however, who, as far as I am aware, practically applied this principle. But I cannot better convince you of the great saving effected by the judicious employment of steam in

this process, than by giving you, in Mr. Crum's own words, the particulars of the plan adopted at Thornliebank printworks:—

"A building is employed 48 feet long inside and 40 feet high, with a mid-wall from bottom to top running lengthwise, so as to form two apartments each 11 feet wide. The manner in which they are fitted up will be understood by reference to the drawing.

"In one of these apartments the goods first receive the moisture they require. Besides the ground floor, it has two open sparred floors 26 feet apart, upon each of which is fixed a row of tin rollers, all long enough to contain two pieces of cloth at their breadth. The rollers, being threaded, are set in motion by a small steam-engine, and the goods to be aged, which are at first placed in the ground floor, are drawn into the chamber above, where they are made to pass over and under each roller, issuing at last at the opposite end (on the right-hand side of the drawing), where they are folded into bundles on one (at a time) of the three stages which are placed there. These stages are partially separated from the rest of the chamber by woollen cloths.

"While the goods are traversing these rollers, they are exposed to heat and moisture, furnished to them by steam, which is made to issue gently from three rows of trumpet-mouth openings. The temperature is raised from 80 to 100 degrees, or more of Fahrenheit—a wet-bulb thermometer indicating at the same time 76 to 96 degrees, or always four degrees less than the dry-bulb thermometer. In this arrangement 50 pieces of 25 yards are exposed at one time, and as each piece is a quarter of an hour under the influence of the steam, 200 pieces pass through in an hour. Although workpeople need scarcely ever enter the warmest part of this chamber, a ventilator in the roof is opened when there is any considerable evolution of acetic acid.

"The mordant, as already explained, does not become fully "aged" by this process alone, although as much so as if it had hung a whole day in cold air. It has received, however, the requisite quantity of moisture (about 7 per cent. of the weight of the printed piece), and is thereby enabled, if an iron mordant, to take oxygen from the air, and to become changed (with time) into the sesquiacetate and sesquihydrate of iron. In order to be sufficiently aged, it must be left one or two, or even three days in an atmosphere still warm and moist.

"It had fortunately been ascertained long before, at Thornliebank, that exposure in single folds after moistening was not necessary. Mr. Graham's experiments on the diffusion of gases through small apertures had served to suggest that for the absorption of the small quantity of oxygen required, the goods might as well be wrapped up and laid in heaps. Accordingly, in the operation in question, the moistened goods are carried in bundles into the building on the opposite side of the mid-wall already mentioned, and deposited there upon the sparred floors which are placed there at heights corresponding with the stages in the first apartment on which the goods are folded down. Upon these floors seven or eight thousand pieces may be laid at a time, and

as each piece is 25 yards long, 100 miles is therefore the quantity that can be stored at once. It is necessary, of course, that an elevated temperature, and a corresponding degree of moisture, be preserved in the storing apartments day and night, and 80° Fahr. is sufficient, with the wet bulb at 76°. To effect that object a large iron pipe is placed along the ground-floor underneath, and moderately heated by steam, while a row of small jets in the same position are made to project steam directly into the air of the apartment. The whole building is defended from external cold, and consequently from condensation of steam, by a warmed entrance room, and by double windows and double roof. Small steam pipes are also placed at other points where they seem to be required; and the apartment with rollers is specially heated, when not in use, by a couple of steam pipes, which are placed under the ceiling of the ground floor.

"The process of ageing, as thus detailed, was in operation at Thornliebank, in the autumn of 1856. About a year afterwards it began to be adopted by other printers, and now it is already in use at at least 16 different printing establishments in Scotland and in Lancashire."

Fourthly, *Dung Substitutes.*—During the last few years the various dung substitutes, such as the double phosphate of soda and lime, the arsenites and arseniates of soda, and the silicates of soda have completely taken the place of cow dung in the process of dunging, that is to say, a process which consists in passing the mordanted and aged cloth into weak and hot solutions of the above-named substances, with the view of fixing thoroughly the mordaunt in the cloth, and removing any excess that may have been used, without allowing it to fix itself on the white or unmordanted parts. By the introduction of these dung substitutes, and improved dunging vats, a great saving of time, labour and expense has been effected. Thousands of pieces are now done in the same vat, where formerly as many hundreds only could be so treated.

Fifthly, *Washing Machines.*— As madder goods have to be thoroughly washed, not only after this operation, but also after dyeing, several improved machines have been introduced into the trade. I shall only here mention those of Messrs. Mather & Platt, Mr. Furnival, Mr. S. Barlow, Mr. D. Crawford, the last of which is much used for steam work and loose colours, and especially that of Mr. Thomas Whittaker, which I have heard highly praised by madder and garancine printers. To give you an idea of the vast capabilities of some of those machines, I will cite the following fact mentioned by Messrs Whittaker: —"Our machine will wash 6,000 yards for all kinds of dyeing purposes, and 12,000 yards for all bleaching purposes, per hour (which only requires the attention of a person of 12 or 14 years of age)."

Sixthly. After the madder goods have undergone the above improved processes they are ready for the dyebeck, where the mordaunts assume the colours for which they are adapted. Here, also, a slight improve-

ment has been effected, the advantage of which is a saving of time; as it now requires for saturating the mordaunts with alizarine or purpurine only $1\frac{1}{4}$ hours for garancine, and 2 hours for madder. After leaving the dyebecks the pieces are thoroughly washed in the improved washing machines, but as the white parts (or those not mordaunted) are still soiled and the colours dim, it is necessary to pass the pieces for half an hour into a rather strong soap solution heated to 180°, when the loose dye is not only removed from the white parts, but also from the parts on which colour has been fixed. To finally brighten the colours and completely clean the white portions, the pieces are passed into a weak solution of what is called "chimic," or an alkaline-hypochlorite of soda, with a little sulphate of zinc, until the desired effect is obtained, but latterly this process has been improved by passing the goods rapidly into chimic and then through a steam chest. As the pieces have not yet, however, a commercial appearance, they further undergo what is called finishing, that is, the pieces are passed through a solution of sour flour (flour which has been fermented for several weeks), starch, farina, &c., and then between rollers, dried, and lastly through calenders, the object of which is to fill up the interstices of the fabrics and to give them a glossy appearance. Much improvement has also taken place in this department of printing by the introduction of new machinery, especially in the methods of adapting the finish to the various markets of the world. I wish to take the opportunity of impressing upon printers the importance of dispensing, as much as possible with the use of sour flour, and confining themselves to that of starch or farina, with the addition of about 1 ounce of sulphate of zinc per piece, for the purpose of diminishing the risk of mildew and other stains, to which a low class of printed goods are liable, during their transit in tropical climates, and especially those dyed with common garancine, bark, sumach, and peachwood.

*Specimens of Madder Styles.**

Of late Mr. Emile Kopp's purpurine and alizarine have been introduced with great success as substitutes for several styles of madder, and the specimens here annexed will show how successful the application of these new colouring matters has proved.

* Supplied by Messrs. Symonds, Cunliffe & Co.

The following are the instructions given by Messrs. Schaaff & Lauth, for the application of these new colouring matters :—

Purpurine dyes with great facility, and at a very moderate temperature ; the bath is perfectly clear, and may serve until exhausted. Upon calico, red and black mordants are dyed very quickly ; a weak soap bath of from 112° to 120° restores the whites and brightens the colours. Violet mordaunts take the colour with the same facility, but the shades are grayish.

To fasten purpurine colours and preserve the whites it is necessary to mix with the purpurine 15 to 20 times its weight of bran and a sufficient quantity of water, at about 104°, and add it to a bath at about 130°, which is then heated so as to boil in about 3-4ths of an hour, and kept boiling for another 3-4ths of an hour, during which the pieces are passed into it, and afterwards into a boiling bran bath, after which a simple washing will suffice to render the whites perfect.

To prepare a steam colour with purpurine for cloth, mordaunted with alumina, the following is the best plan: The purpurine is added to 20 per cent of its weight of carbonate of soda ; the whole being well brayed together, hot rain water is added to it, and a magnificent red solution is obtained, which is filtered and left to cool. It is then thickened with starch to the required consistency, and may be preserved without alteration for a long time. When required it is printed, steamed and washed in cold water. With 20 grammes (about 300 grains) of purpurine per quart, a good colour is obtained.

If in filtering the purpurine solution there is any deposit on the filter, it may be used in ordinary dyeing.

Alizarine.—This colour is used for dyeing upon cotton and calico in the same manner as garancine and flower of madder. Its properties are very similar to those of flower of madder, but the colours are faster.

Upon calico, double and triple violets, with black single and double roses, and Turkey red, are obtained as easily with this product as with any preparation of garancine.

The colours of alizarine possess the great advantage of being acted upon by soap, acid, alkalis, and the salts or solution of tin, without losing intensity, and at the same time they gain in brilliancy ; it is therefore necessary to use an eighth or tenth less of the mordaunt, to avoid obtaining deeper shades than would be produced by garancine or flower of madder.

In dyeing with alizarine it should be moistened with warm water before being placed in the bath, otherwise it will float, and, perhaps, stain the cloth.

As alizarine does not part with its colouring principle at a lower temperature than from 105° to 120°, it is not necessary to pass the goods into the bath below 85° to 90°, but it is better to keep them at that heat two hours before proceeding to the boil.

The brightening of the various colours dyed with alizarine is done in the same way as for garancine, &c., but as the whites remain better, less soaping is required.

Lime has a great affinity for alizarine, and it is therefore necessary to attend to the purity of the water used, neutralizing it, if required, with oxalic acid.

*Purpurine.** *Alizarine.** *Purpurine.**

The process for producing Turkey-red on fabrics being identical with that for yarns (already described in my first lecture), it is unnecessary to repeat here the details of the process, But besides the intricate and difficult manipulation which Turkey-red goods have to undergo, there is another peculiarity connected with them, viz., the method by which the whites are obtained, which is the reverse of that followed with madder goods, in which the whites are preserved, whilst in the case of Turkey-red the whites are obtained by destroying the colour after it has been fixed. This is done by printing tartaric acid on the cloth, and then bringing it into contact with bleaching liquor (or hypochlorite of lime), or by forcing a weak solution of sulphuric acid and bleaching powder through perforated plates, the result being that the red is destroyed on those parts where the acid and bleaching liquor have come in contact with the fabric.

In the last Exhibition there were some beautiful examples of plain and printed Turkey red fabrics exhibited by the following firms :—

United Kingdom.—H. Monteith and Co., J. O. Ewing and Co., W. Stirling and Sons.

France.—C. Steiner.

Russia.—A. Baranova.

Switzerland.—Luchsmejer, Elmer, and Oertli (367).

I wish specially to state with reference to the Turkey-red goods exhibited by the above Scotch houses, that they have succeeded in retaining among them a large share of this important manufacture, which has disappeared from some districts where it had originally attained its greatest renown.

The last improvement which I am aware of in this branch of manufacture is that invented by Mr. Horace Koechlin, who has lately published a simple method for obtaining a blue or a green, by means of

* Supplied by Messrs. Schaaff & Lauth.

a compound of iron and lead. A lead mordaunt is fixed on the fabrics by means either of ammonia or sulphate of soda, the fabric being further padded in a weak solution of either silicate or arseniate of soda. The pieces are then padded at a temperature of 140° in a beck containing 200 gallons of water, six pounds of sulphate of protoxide of iron, and three ounces of protochloride of tin. The pieces are washed and then passed into a second bath, composed of 200 gallons of water, 15lbs. of yellow prussiate, with 3lbs. of sulphuric acid, after which they are washed and dried. By this process the ground of the piece is blue, and wherever there is lead green is produced.

Indigo.—Most of the styles obtained with this valuable dye-stuff are due to the mixture of printing and dyeing, and only a few improvements have been effected herein, to my knowledge, during the last ten years.

First, the usual method of dyeing cotton, plain or self blue, is to fill with water large stone vats, and dissolving in them two parts of sulphate of protoxide of iron, adding one part of finely ground indigo, and then three parts of hydrate of lime. After having well stirred the whole for several hours, pieces of calico which have been hooked on a frame and dipped in lime water, are then plunged for 15 minutes into the vat, when the blue indigo which has been converted into white indigo by the protoxide of iron, and rendered soluble by the excess of lime, fixes itself on the fibre, and, on the exposure of the latter to the atmosphere, re-absorbs oxygen and becomes blue. When white patterns are required, the pieces are printed before dyeing with what is called a "reserve," that is, a composition which prevents the colour from fixing itself on the fibre; the chief ingredient for that purpose is sulphate of copper, which acts by prematurely oxydising the indigo, and thus preventing its fixation. In both these cases the pieces are passed through a weak sulphuric acid bath to perfectly fix the indigo, and formerly the copper thereby liberated from the fabrics was completely lost. Mr. Joseph Leese has recently devised a method of saving this valuable metal. To effect this, the diluted solution of sulphate of copper is made to filter through vessels containing wrought-iron turnings, the acid thus dissolving the iron, which may be used as sulphate of protoxide of iron for future operations, whilst the copper deposited on the excess of iron employed may be used, if thought fit, to manufacture again sulphate of copper. To give an idea of the importance of small savings, I may state that this ingenious, but apparently trifling improvement, saved at least £3,000 a-year to one firm.

Secondly. A few years ago I was also able to effect an economy in this branch of calico printing, which consisted in extracting from the cold indigo vats which were considered by the printer to be exhausted, a considerable percentage of the indigo originally employed. Having observed that a green insoluble flocculent matter, which remained in the vats, and which was considered by chemists and printers to be simply oxide of iron, was in reality a compound of indigo and iron, I

devised the following simple means of extracting the indigo therefrom:—The green pulp alluded to was conveyed from the several exhausted indigo vats into a general receptacle, and there mixed, first with a small quantity of hydrochloric acid, so as to remove the excess of lime, allowing the green pulp to settle, and running off the liquor. The so purified green pulp was then treated with strong hydrochloric acid, when chloride of iron was produced, and the indigo liberated, which required only to be washed to become again fit for use.

Thirdly. Although the printing of indigo offers great difficulty, still several printers have recourse to it from time to time, with greater or less success. The usual method of printing indigo consisted in mixing finely-powdered indigo with orpiment, or protochloride of tin, with a caustic alkali, and this process was further facilitated by printing the pieces in an atmosphere of coal gas, as devised by Mr. Bennett Woodcroft, the present learned officer of the Great Seal Patent Office, and carried out by Messrs. T. Hoyle and Sons, of Manchester. But of late years Mr. Joseph Leese, of Messrs. Kershaw, Leese, and Co., has succeeded in applying the following method, first devised by Mr. Fritzsche. The indigo is finely ground, and reduced to an impalpable powder, and then mixed with glucose, lime, and caustic soda, in such proportions as are needed to produce the shade of colour required. These materials are all mixed cold, and after the cloth is printed with the mixture it is passed through a steam chest, in which it is exposed for the space of from 30 to 60 seconds. In this short period the indigo is completely reduced and rendered soluble, when it enters into the fibre, and on emerging from the steam chest it becomes oxydised and fixed by exposure to the atmosphere, or the pieces may be immersed in a solution of an oxydising agent, such as dilute sulphate of copper, after which they only require to be washed, dried, and finished.

I am not aware of any marked improvement in the style of printing called "spirit colours," but in that of "steam colours" considerable advance has been made since 1851, rather, however, in a mechanical and artistic, than in a chemical point of view on the other hand. Still it is so largely used at the present day, especially in producing furniture prints, it is desirable to give an outline of its chief characteristics. Either the colour is mixed with a mordaunt and then printed on the cloth and submitted to the action of steam in a close chamber or over a perforated cylinder, or the pieces are passed through a tin solution, the oxide of tin being precipitated on the fabric by a chemical process, when the colour, properly thickened, is printed and afterwards submitted to the action of steam. It is chiefly by this style of printing that such fine effects are produced upon mixed fabrics of cotton and wool. It was owing to certain mechanical improvements that Mr. Robert Kay, calico printer, of Manchester, and his workmen, had the honour of obtaining the gold medal at the Paris Exhibiton of 1855. The beautiful furniture patterns which he exhibited there were the result, not only of artistic skill, and of improved machinery, by which twenty

colours can be printed at once, but also an invention patented by Mr. K. Burch, of Macclesfield, of which Mr. Kay availed himself with great tact. Of course you must be aware that, in order to produce light shades of colour, the darker shades are diluted with gum water, or reduced liquid; this was the work of the colour mixer, and, therefore, to produce four colours and four shades of each colour, sixteen rollers would be required. Now the invention of Mr. Burch consists in reducing the colour upon the cloth during the process of printing. The pattern of the paler shades of each colour in a chintz design being engraved on one roller, an impression in gum-water or reducing liquid is given off upon the cloth first, the impression of the other rollers then following in the usual order; where the different colours fall upon the gum-water a lighter shade is produced, owing to the dilution of the colour on those parts, which effect may be still further heightened, by more lightly engraving the corresponding parts of the colouring roller, so that a less quantity of colour shall be given off. The application of this process to furniture styles, first by Mr. Kay, and of late by Messrs. Littlewood and Wilson, and other large printers of Manchester, together with the substitution of the large rollers above mentioned, for block printing, has produced quite a revolution in furniture styles, of which fine specimens were seen at the last Exhibition. By the adaptation to this style of the "pigment" principle, some French houses exhibited some most magnificent examples of furniture printing, of which I noticed especially those of Messrs. Thierry Meig, and Huguenin Collineau.

The introduction of the tar colours has enabled the woollen and silk printers to obtain, with the aid of steam, most excellent effects, by which many of them, chiefly foreigners, have displayed a great variety of very beautiful specimens, this being particularly noticeable in the production of cheap and elegant goods, principally shawls, in the Prussian and Austrian departments. I also admired some fine specimens of steam work on mixed fabrics for ladies' dresses in the exhibit of Messrs. Leitenberger (Austria), and the Rossendale Printing Company, Manchester.

Pigment Printing.—This style remained for many years in a dormant condition, owing, firstly, to the insufficient varieties of pigments, and secondly, to the difficulty of finding a proper fixing agent, for it was necessary to find a substance which would give the pigment the required consistency, and at the same time cause it to adhere to the cloth. In 1843 india-rubber dissolved in naphtha was proposed as a fixing agent for artificial ultramarine, but owing to the danger of fire, and for other reasons, this method was abandoned. In 1847, egg albumen was introduced into this country for the same purpose, but owing to the coarseness of the ultramarine, and its high price, which was about £8 per lb, (it is now 1s. 3d.) the progress of this mode

Ultramarine.

of printing was greatly retarded. In 1849, Mr. R. T. Pattison, of Glasgow, patented the use of caseine from milk, which he called lactarine, which promoted the use of ultramarine, buff, and stone pigments in shawl printing. About the same period, another fixing agent was introduced, viz., albumen obtained from blood. The style of pigment printing, however, received an extraordinary impetus in the spring of 1859, when the purple aniline of Mr. Perkin was successfully introduced by Messrs. James Black and Co., of Glasgow, and the French purple of Messrs. Guinon, Marnas, and Bonnet, of Lyons, by Messrs. Walter Crum and Co., Dalglish and Co., Boyd and Hamel, Inglis and Wakefield, Heys, &c., who obtained the splendid mauves and purples which astonished the world by their beauty, fastness, and brilliancy, by printing albumen or lactarine on muslin, and fixing the same by coagulating it by the action of steam. The pieces were then passed into the dyebeck, containing in solution Mr. Perkin's aniline purple, or Messrs. Guinon, Marnas, and Co.'s French purple, first dissolved in oxalic acid, and then added to a slightly ammoniacal bath, when the albumen or lactarine took up the colour and fixed it on the cloth, the pieces being then thoroughly washed, to remove any excess of colour. In the middle of the same year, a beautiful green pigment, which had been patented in 1858, by Mr. Guignet, was introduced, and as it is extensively employed, it may be interesting to know how this green oxide of chrome is produced. Three parts of boracia acid are intimately mixed with one part of bichromate of potash and a sufficient quantity of water to form the whole into a thick paste. It is then introduced into a furnace, and heated to a dull red heat, when a borate of potash and a borate of oxide of chrome are produced. The mass is allowed to cool, and is then thrown into cold water, when the borate of potash dissolves, and the borate of oxide of chrome is decomposed, the hydrate of oxide of chromium, $C_2 O_3 + 3HO$, falling to the bottom as a magnificent green powder, which requires only to be well washed and drained to be ready for use. The peculiarity of this green, as well as of one prepared by Mr. Arnaudon, of Turin, from phosphate of ammonia and bichromate of potash, is that, besides being of a brilliant green, they maintain this colour by artificial light. In the last Exhibition I noticed some very fine intensely dark green pigment on some muslin fabrics, and on inquiry, found that it was produced by a German chemist, and was assured that it was a cyanurated compound of chrome, corresponding in composition to Prussian blue, the chromium being substituted for iron.

French Purple.

Guignet's Green.

In the month of November, 1859, the magenta colour, or fuchsine, of

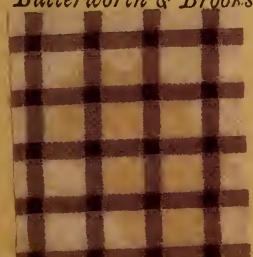
Messrs. Renard, was also introduced to the printing trade, and fixed by the above described method. The beautiful pinks thus obtained were soon followed by the application of roseine, azaléine, and other aniline reds. In May, 1859, a further improvement was made, which reduced the cost of applying these colours to muslins, by Mr. Walter Crum, who made the curious observation that if the gluten of wheaten flour is allowed by exposure to the atmosphere to fall into a semi-fluid condition, it is easily dissolved in a weak solution of caustic soda, which solution he used as a substitute for albumen or lactarine. About the same time, Mr. Scheurer-Kestner also introduced the use of gluten by the aid of weak acids, and Messrs. W. A. Perkin, and Matthew Gray, of the Dalmarnock Printing Company, proposed to fix the coal tar colours on fabrics by means of a lead soap, already referred to in my previous lecture.

Early in 1860 calico printers succeeded in printing the aniline colours directly with the animal mordaunts, instead of dyeing the mordaunts after the latter were printed and fixed, and thus were enabled not only to print a variety of colours on the same piece, but also to effect a great saving and simplicity in the operation. By this means the pigment style was fully developed, and an entirely new class of prints was introduced into this market.

Pigment Printing.

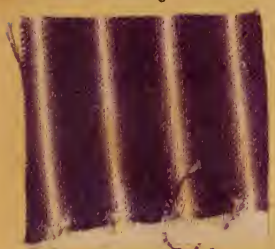
Owing to the great extension of this style, the cost of the animal mordaunts became such a serious consideration as to cause anxious search for other means of fixing the colours, and Mr. Charles Lowe and myself having observed in 1856 that tanning matters would precipitate and render insoluble certain coal-tar colours, and having further observed, at the end of 1859, that tannin, when printed on cloth and submitted to the action of steam would become fixed, and serve as a mordaunt for coal-tar colours, we took out a provisional specification on the 10th of December, 1859, for fixing the insoluble tanning compound formed by adding a solution of gall-nuts, to a coal-tar colour, on cloth prepared with oxide of tin or alumina, or other metallic oxides. For various reasons this patent was not proceeded with, but in the early part of 1861 Mr. Gratrix, with the intelligent and persevering assistance of Messrs. Butterworth and Brooks, of Manchester, succeeded in fixing aniline purples, which, though faster against soap than those printed with albumen, did not so perfectly resist the action of light. The first process used by Mr. Gratrix was, with a very slight modification, the same as that described above, but his second process, which I think he preferred, was the following:—he took cloth prepared with oxide of tin, such as is generally used for steam colours, and after having printed it with a gall-nut

Aniline fixed by Messrs. Butterworth & Brooks.



solution, submitted it to the action of steam, when the tannin became fixed and insoluble; the pieces were then passed through a dunging liquor, washed, and then into a beck containing aniline purple mixed with a little acetic acid. As the bath was gradually carried to the boil, the colour fixed itself on the tannin, and thus produced the print, but as the whites were rather soiled, the pieces were passed into a weak acid bath, or through a weak solution of printing clearing liquor, such as is used for garancine.

Aniline fixed by Messrs. Littlewood & Wilson.



Early in 1860, Mr. John Lightfoot also took out a patent to fix colours, especially those from coal-tar, by various means, the chief of which was tannate of gelatine. In 1861 patents were secured by Messrs. Pattison, Miller, and Nathaniel Lloyd, and J. G. Dale. The last of these patents is, in my opinion, one of the best which have been taken out for that purpose, and is successfully worked by Messrs. Littlewood and Wilson, of Accrington.

I cannot do better than give this extract from their patent:—

"Our invention consists in an improved method of fixing that class of colours derived from aniline, naphthaline, &c. (known under the names of mauve, magenta, rosaline, roseine, &c.) upon cotton or linen materials or fabrics. In order to accomplish this object we mix tannin with the colour to be printed, and thicken it with gum senegal or any other appropriate thickening. This colour is printed upon unprepared goods, steamed, and passed through a boiling solution of tartarized antimony; or we print on tannin alone thickened with gum senegal, steam, and pass through the antimony solution, and afterwards dye the cloth in a weak solution of mauve or other aniline colour, which solution we prefer to be used with acetic acid. When we desire to use the first-mentioned process we take a colour compound as under,—

1 gall. gum water, 8 to 10 oz. of pure tannin.
Coloring matter to shade required.

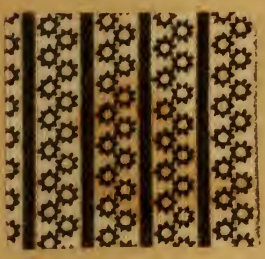
This is then printed upon unprepared goods, steamed at a pressure of from ¾lb to 1lb. per square inch, and passed through a bath of tartarized antimony of the strength of about 2 oz. per gallon of water, at a temperature of from 180° to 212° F. After passing through this solution the goods are washed, dried, and finished in the usual manner.

Mr. Emile Kopp has lately published an interesting paper on the tannate of rosaniline, which although insoluble in water is soluble in acetic acid, and thus is susceptible of application, for after the application of this solution on a print, its solvent (acetic acid) is easily driven off by steam, and the tannate of rosaniline is fixed on the fabric. Strong alkalies and acids decompose this product, and therefore spoil the colour. Mr. Kopp has further made the interesting remark that when tannate of rosaniline is mixed with wood spirit containing but a small quantity of acid, its colour changes from red to purple, and then to

blue; a gentle heat facilitates this curious transformation. This blue can be precipitated from its alcoholic solution by the addition of a small quantity of carbonate of soda. The alcoholic solution can be employed for dyeing silk and wool, but the shades are not sufficiently brilliant to compete with those of azuline or bleu de Lyon.

Although it has been long known to chemists that aniline would yield a green colour when submitted to the action of certain oxidizing agents, up to the present time all efforts to dye silk or wool commercially with it have failed; but in 1860, Messrs. Calvert, Clift and Lowe, introduced a most easy and practical method of producing it, under the name of *emeraldine*, on cotton fabrics, specimens of which were exhibited in the chemical department.

Emeraldine.



The process consists in printing an acid chloride of aniline on a cotton fabric prepared with chlorate of potash, and in a few hours a beautiful bright green gradually appears, which only requires to be washed. If the green fabric is passed through a solution of bichromate of potash, this colour is transformed into a dark indigo blue, called *azurine*.

The production of this colour directly on the fabric is most important, and it will probably lead to the similar production of the other coal-tar colours, without previous treatment, directly on the cloth. By this means not only the great loss of aniline in the original production of the colour will be avoided, but a considerable economy of mordants will be effected.

These gentlemen also induced Messrs. Wood and Wright at the end of 1860 to produce by their process dark green or blue, which they considered sufficiently good to be introduced into the market, and Messrs. Wood and Wright have further effected an improvement in these dark shades, which may be called black, by adding to the chlorate of potash persalts of iron, or other oxydising agents; also by oxydising the colour thus produced on the fabric (which is the chief novelty of this process),

Aniline Black.

either by a weak solution of bichromate of potash or bleaching powder. Nitrate of copper may be mixed with the hydrochlorate of aniline, without the addition of chlorate of potash, and the mixture printed on the fabric, when gradually a dark green or black is produced. This mode of printing directly on the fabric gives green or blue, so dark as to be almost identical with black.

Dark blues imitating indigo have also been produced on a commercial scale by this process, and its success was such that if the colour had not been affected by acids, it would have superseded most of the indigo styles.

A most interesting and valuable method of applying aniline colours on fabrics has been devised by M. Onfroy, of Paris. It consists in

printing the aniline red, purple, or blue, on a solid black or brown ground, in which gallic acid has been used instead of the ordinary tanning matters, the result of which is, that the black or brown ground is more easily reduced, so that if he mixes with the aniline colours and animal mordaunts some acid, such as oxalic acid, the black or brown is destroyed, and the aniline colour fixed.

It is to be regretted that the beautiful colours obtained from coal-tar should be exposed to injury in public estimation, owing to certain parties printing them with starch only, by which they are so loosely attached to the fabric, that a slight washing in pure water will entirely remove the colour and leave nothing but white cloth. By such means the reputation of this style of printing is being rapidly destroyed, and these colours, which might otherwise become a valuable addition to the printers' repertoire, are likely to lose altogether the favour of the public. This subject is so important that I cannot refrain from making another remark, viz, that if the use of coal-tar colours were properly encouraged, they would doubtless gradually decrease in price, and this country, instead of being tributary to others for its dyestuffs, would in time become the purveyor of dyeing materials, or of the substances yielding them, to the whole world.

I cannot conclude this paper without calling your attention to the immense extent to which calico printing is carried out, and the wonderful progress it has made. Thus in 1830 about 200,000 pieces were printed. In 1851, according to a lecture delivered before this society by Mr. E. Potter, M.P., the estimated quantity of goods exported was 6,465,000 pieces, and the same authority estimates that in 1857 the export of printed calico amounted to about 27,000,000 pieces.

*** The optical apparatus for detecting madder colours (mentioned in page 7) may be obtained of Mr. G. Dancer, Cross Street, Manchester.

Specimen of Picric Acid—(omitted in its proper place.)

Palmer and Howe, Printers, Bond Street, Manchester.

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